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ROLE OF BINDERS IN SOLID PROPELLANT COMBUSTION

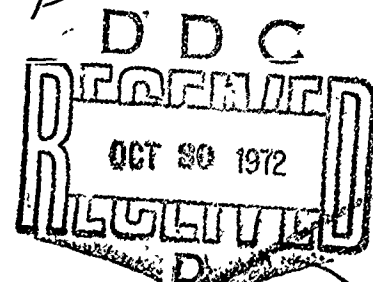
N. S. COHEN AND R. W. FLEMING
LOCKHEED PROPULSION COMPANY

TECHNICAL REPORT AFRPL-TR-72- 96

OCTOBER 1972

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AFRPL-TR-72- 96

LPC REPORT NO. 570-F

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ROLE OF BINDERS IN SOLID PROPELLANT COMBUSTION

**N. S. COHEN AND R. W. FLEMING
LOCKHEED PROPULSION COMPANY**

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FOREWORD

New
This is Lockheed Propulsion Company (LPC) Technical Report 570-F, issued under Contract F04611-71-C-0061 and submitted 25 August 1972. Reported herein is research conducted between 14 June 1971 and 16 June 1972. The authors are N.S. Cohen and R.W. Fleming. Contributions to the technical effort were made by R. L. Derr, R.H. Epstein, W.E. Heikkila, and S.E. Peterson. These personnel are members of the Research Branch of LPC (1500 Crafton Avenue, Redlands, California 92373) under the direction of J.H. Bonin.

Work performed under this contract was monitored by the Air Force Rocket Propulsion Laboratory (AFRPL), Edwards, California. The Project Engineer is Capt. Leigh E. Stamets, AFRPL/DYSC.

This technical report has been reviewed and is approved.

Leigh E. Stamets, Capt., USAF
Project Engineer

ABSTRACT

The objective of this program was to investigate and define the effects of inert binder properties on composite solid propellant burning rate. Experimental pyrolysis data were obtained for many binders of practical interest over a wide range of heating rates and pressures, in several environmental gases, with and without 10-percent ammonium perchlorate (AP) contained in the sample, and in some cases with burn rate catalysts. These data were used to extract kinetics constants from Arrhenius plots, and heat of decomposition. In addition, motion pictures were taken of the pyrolyzing surface and gas samples were extracted for analysis. Pyrolysis kinetics varied between binders, but were found to be independent of pressure, the presence of AP, and the presence of catalysts; however, a chlorine gas environment had a material effect upon the results. All of the binders exhibited molten, boiling surfaces mingled with char, to varying degrees; the amount of char increased with AP present, and in chlorine. Relevant data were input to the Derr-Beckstead-Price combustion model in order to associate binder properties with known binder effects on burning rate. Although the effects were predictable, they stemmed from properties other than pyrolysis kinetics; however, the binder data applied to the model revealed possible deficiencies in the model, which are discussed. It appears that the approach of combustion tailoring by binder modification would have to involve the gas phase combustion processes rather than surface pyrolysis. Therefore, future work concerning the role of binder should be directed toward the gas phase.

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SECTION I

INTRODUCTION

The evolution of composite propellants based upon ammonium perchlorate (AP) and aluminum reflects the chemist's ability to improve the binder network that combines these materials into a useful matrix. The history of propellant binders has been a result of developments available from the polymer and plastics industries. From these areas, the propellant industry has adopted selected materials and, through essentially an empirical approach, has produced binder systems that can provide the desired propellant physical and chemical properties. In this regard, propellant binder selection and evaluation has been essentially dictated by physical property requirements and the desire for maximum energy release. The role of the propellant binder in the combustion process has been given low priority during the development of these materials, and it is in this area that significant progress needs to be made for an understanding of the effect of binder type and composition on solid propellant burning rate.

In practice, the inert binders used in production composite propellants over the past 15 years have only secondary effects on burning rate. At a time when propellant technology limited oxidizer particle size selectability, total solids, and use of additives, this secondary effect was sufficient to base binder selection on burning rate in some instances (other factors being about equal). As propellant technology made available a variety of approaches for combustion tailoring, the secondary effects of binder on combustion were overcome and attention to the more classical binder requirements was emphasized (e.g., HTPB developments). However, the alternate approaches for combustion tailoring proved inadequate in certain specialized areas, such as extinguishability, and binder selection has been predicated on extinguishability for controllable motors (1-3). Also, as the alternate approaches become saturated as to effectiveness (e.g., AP particle size approaches zero), and as certain disadvantages are encountered in their use (e.g., catalyst migration), the need arises to address binders as a potential source for major combustion tailoring effects. That this approach is feasible is demonstrated by the major combustion effects brought about by certain polymers used in specialized R&D programs (3-7); it has been recognized in various attempts to weave certain compounds into the polymer network (8, 9).

Compared to the considerable effort directed toward improved understanding of the role of AP in propellant combustion, little attention has been given the binder. Available research concerning the pyrolysis, oxidation, and burning of polymers has emphasized materials that are not used as propellant binders, and/or experimental methods that are not representative of propellant combustion conditions (10, 11). Therefore, use of this information to postulate mechanisms, formulate or implement analytical models, or propose empirical tailoring approaches, would be open to question. In June of 1970, a group of analytical and experimental researchers met at San Diego, California, as a JANNAF-sponsored workshop to review steady-state combustion and modeling of composite solid

propellants (12). It was pointed out that there is a need for experimental data not only to implement existing models, but to validate models concerning the role of binder in the overall combustion process.

In June of 1971, the Air Force Rocket Propulsion Laboratory (AFRPL) contracted Lockheed Propulsion Company (LPC) to embark upon an experimental program to study the mechanistic role of binder in composite solid propellant combustion. Emphasis would be placed upon:

- Studying materials used in solid propellants
- Acquiring quantitative pyrolysis data, due consideration given to validity of technique
- Acquiring qualitative information of surface characteristics, seeking evidence of melting, boiling, sublimation, or heterogeneous reaction in the sense of oxidative polymer degradation
- Evaluating the Derr-Beckstead-Price model in the light of the experimental data acquired
- Relating the experimental data, with and without the model, to known burning rate effects

Given a valid model, required input data, model computations, and knowledge of how binder variations produce burning rate effects to varying degrees, the mechanistic role of binder can be better defined for future exploitation in combustion tailoring.

SECTION II

SUMMARY

1. BINDERS

Experiments were performed with CTPB, HTPB, PBAN, polyurethane, polysulfide, fluorocarbon, and carborane binders. Two versions of CTPB, HC-434 and Butarez II, were employed. Two versions of HTPB, unsaturated R-45 and saturated Telagen, were employed. Additional variations in HTPB included incorporating additives in concentrations representative of propellant. These materials encompass a wide range of burning rate effects in practical binders

For each binder, an additional batch was made containing 10-percent AP.

2. EXPERIMENTAL CONDITIONS

The major experimental effort consisted of acquiring pyrolysis data over a wide range of conditions. The energy source was supplied by a xenon arc-image furnace. Principal data acquired were mass loss and surface temperature, resulting in the generation of Arrhenius plots to determine pyrolysis kinetics, and energy balance plots to determine heat of decomposition in conjunction with measured thermal properties. Motion pictures of the pyrolyzing surface also were obtained.

Testing encompassed the following range of conditions:

- Heat flux: 3 to 220 cal/cm²-sec, with emphasis on the range of 15 to 200
- Pressure: 1 atmosphere to 1000 psi N₂, 3 psia to 1 atmosphere Cl₂, and 7 psia air
- Exposure times: 125 milliseconds to 7 seconds, decreasing in magnitude and range with increasing heat flux

Samples of pyrolysis products were taken for analysis at 100 cal/cm²-sec and 1 atmosphere of N₂.

3. EXPERIMENTAL RESULTS

For a given binder, there were no effects of pressure, the presence of AP, or the presence of catalysts on the Arrhenius plot for pyrolysis generated by varying heat flux. Variation in heat flux produced the significant variations in mass loss and surface temperature necessary to construct the plot. Polyurethane exhibited the greatest mass loss rates and lowest surface temperatures (768°C at 200 cal/cm²-sec); fluorocarbon exhibited the lowest mass loss rates and highest surface temperatures (2550°C at 200 cal/cm²-sec). Activation energies varied between the binders, but were

less than 17 kcal/mole, indicating a weak-link decomposition mechanism or a physical process such as boiling. The ratio of the activation energy to the logarithm of the prefactor was similar for all the binders, indicating similarity in mechanism, but was higher for fluorocarbon and carborane (these have the common feature of applications in the area of thermal resistance, e.g., insulations, high-temperature paints, etc., notwithstanding diametrically opposed burning rate effects in propellants). Heat of decomposition was lowest for polyurethane (260 cal/gm), and highest for fluorocarbon (1004 cal/gm). Other thermal properties were similar between the binders.

A chlorine environment produced significant effects upon the pyrolysis results, which varied with different binders. In general, the effect was to shift the Arrhenius plot to regions of lower mass loss and higher surface temperature. With *n*-Butylferrocene (nBf), however, the mechanism appeared to be a function of heat flux, and in fluorocarbon containing AP, the chlorine enhanced pyrolysis at higher heat flux. It is not certain that a true heterogeneous reaction was being measured, because of the possibility of gas phase reactions. Gas phase reactions were observed at 1 atmosphere, but did not appear to occur at 3 psia or the selected test pressure of 7 psia. Air also had an effect upon the pyrolysis, but not as dramatic as that of chlorine.

Motion picture observations of the pyrolyzing surface demonstrated that all binders decompose through a molten and boiling surface mingled with carbonaceous residue. The amount of char and black smoke evolved tends to increase with heat flux, with the presence of AP, and with chlorine. The appearance of the molten layer varied from watery for polyurethane to tar-like for fluorocarbon. With increasing pressure, the boiling bubbles appeared smaller; at 1000 psi, the smoke evolved became white, intermingled with globules of heavy brownish smoke, and with AP present there were puffs of white smoke. The only differences between the binders were in degree rather than kind; an exception was the carborane binder, which exhibited a white residue that was modified in physical-texture by the presence of AP.

Mass spectrographic analysis of pyrolysis products revealed a broad array of mass numbers dominated by heavy hydrocarbons. Mass numbers 82 and 84 consistently gave greatest intensities. The mass number distributions were rather similar despite the wide array of polymer structures tested. However, many products predicted by thermochemical equilibrium (e.g., CH_3 , CH_4 , H_2O) did not appear.

4. APPLICATION OF THE COMBUSTION MODEL

The quantitative data were input to the Derr-Beckstead-Price combustion model and were applied to several unmetallized research propellants showing binder effects on burning rate. The effects were correctly predicted. However, it was determined that the effects were due principally to flame temperature differences that arise at lower AP concentrations between binders having differing oxygen contents. These differences are mitigated in practical propellants of high solids loadings and with metal.

Another consequence of research propellants having sufficiently low AP concentration is the appearance of a mesa in the burning rate curve. The model predicted this behavior, and showed that it results from impeded diffusion. Another explanation that has been proposed is physical interference with AP resulting from binder melting. A physical model of melting is not contained within the present model. Although it is now established that all binders of interest do melt, the need for such a physical model would depend upon its importance.

The data provided binder kinetics prefactors that were considerably lower than assumed previously in model calculations. The consequence was an unrealistic prediction of the propellant surface structure during burning. It is believed that the model should be modified to allow for different AP and binder surface temperatures to correct this deficiency. However, further study revealed that the impact of this deficiency on the burning rate prediction would be minor.

A problem was encountered in applying the properties of fluorocarbon propellant, which was traced to the diffusion equations. The unique stoichiometry of fluorocarbon (it contains the most oxidizer) caused the equations to enter a physically forbidden regime wherein negative diffusion distances and flame heights were predicted. The consequence was unrealistic burning rate predictions. Blocking this regime by a program statement resulted in the prediction of two unique characteristics of fluorocarbon: the uniform high pressure exponent and the independence of burning rate on particle size. A reexamination of the diffusion model is in order for application of the model to binders containing appreciable oxidizer in their structure; perhaps extension of the model to active binders is also in order.

The model indicated that the role of binder in the gas phase combustion processes is the effective route for major combustion tailoring, rather than in surface decomposition processes. Extreme variations in surface decomposition kinetics have at most a minor influence on burning rate; binder heat of decomposition has a larger effect but still secondary, as evidenced by the predicted result for the saturated polybutadiene. Catalytic effects could not be predicted from surface processes associated with the binder because the results of this program did not provide a basis for doing so.

5. CORRELATION OF DATA AND BINDER PROPERTIES WITH BURNING RATE INDEPENDENT OF THE MODEL

Attempts to relate binder properties to burning rate trends, apart from use of a combustion model, did not provide concrete information. The flame temperature correlation is certainly evident, but is limited to hydrocarbon binders and special formulations used in research. Kinetics properties, polymer structure, and burning rate trends could not be interrelated. Catalysts could not be related to high burning rate trends since no effect of catalysts was observed on this program, except under circumstances where flame processes may have appeared (ignitions with AP at combined high heat flux and pressure, and effects in chlorine).

Fluorocarbon is unique with respect to stoichiometry and the presence of fluorine in an inert polymer structure. The only unique property measured on this program was a high heat of decomposition. Therefore, the relatively low burning rate may in some way be associated with these characteristics.

6. RECOMMENDATION

Future study of the role of binder in solid propellant combustion should be directed toward the gas phase processes.

SECTION III

BINDERS

1. EFFECTS OF BINDER ON BURNING RATE

Several studies have been conducted in which the influence of binder changes on burning rate has been systematically examined (10). A multitude of programs, involving propellant development efforts and largely unreported in the context of binder effects on combustion, have been conducted from which major trends can be inferred by cross comparison. Based on a review of this information, binder effects can be categorized in terms of minor or secondary influences, moderate influences, and major influences.

A summary plot illustrative of the essential trends is presented as Figure 1. Representative catalysts are included inasmuch as they are mixed into the binder, although the effects may not stem from the binder alone.

a. Minor or Secondary Effects

Binders that have been used in production propellants have only secondary influences upon burning rate. What is meant by a secondary influence is illustrated in Figure 1, wherein comparison is made between PBAA, PBAN, polysulfide, polyurethane, polyvinylchloride (ARCITE), and polystyrene (not used in practical propellant)(10); HC-434 CTPB, Butarez CTPB, PBAA, and R-45 HTPB (13); various polybutadiene copolymers and terpolymers (6); and various unsaturated polymers (14). The character of the burning rate-versus-pressure curve, i. e., its basic shape over a wide pressure range, is essentially the same. The differences that do exist are of a more subtle nature. The total width of the burning rate band at 1000 psi represents a burning rate variation of the order of 50 percent. Although the polysulfide propellant shows a higher burning rate than the equivalent PBAA propellant, consideration of total solids achievable, oxidizer particle size, and catalysts in practical propellants enables PBAA propellants to be tailored to have higher burning rates than could be achieved in polysulfide.

Studies have also been reported concerning the effect of curatives on burning rate. In one study using PBAA propellant (6), four different epoxy curatives at four different concentrations were examined. Effects upon burning rate over the range 500 to 2000 psi were mostly within experimental error, and never beyond what would be considered small. In a recent LPC program using CTPB propellant for the NASA (15), propellants were made using mixtures of epoxy and aziridine curatives as well as with either kind alone. The propellants otherwise were identical. Effects upon burning rate over the range 50 to 1000 psi were mostly within experimental error. (A change was eventually made to HTPB binder with the same negligible effect.)

As a practical matter, propellants are manufactured with plasticizers in the binder. Propellant development efforts include variation of the amount and type of plasticizer, but rarely complete elimination thereof.

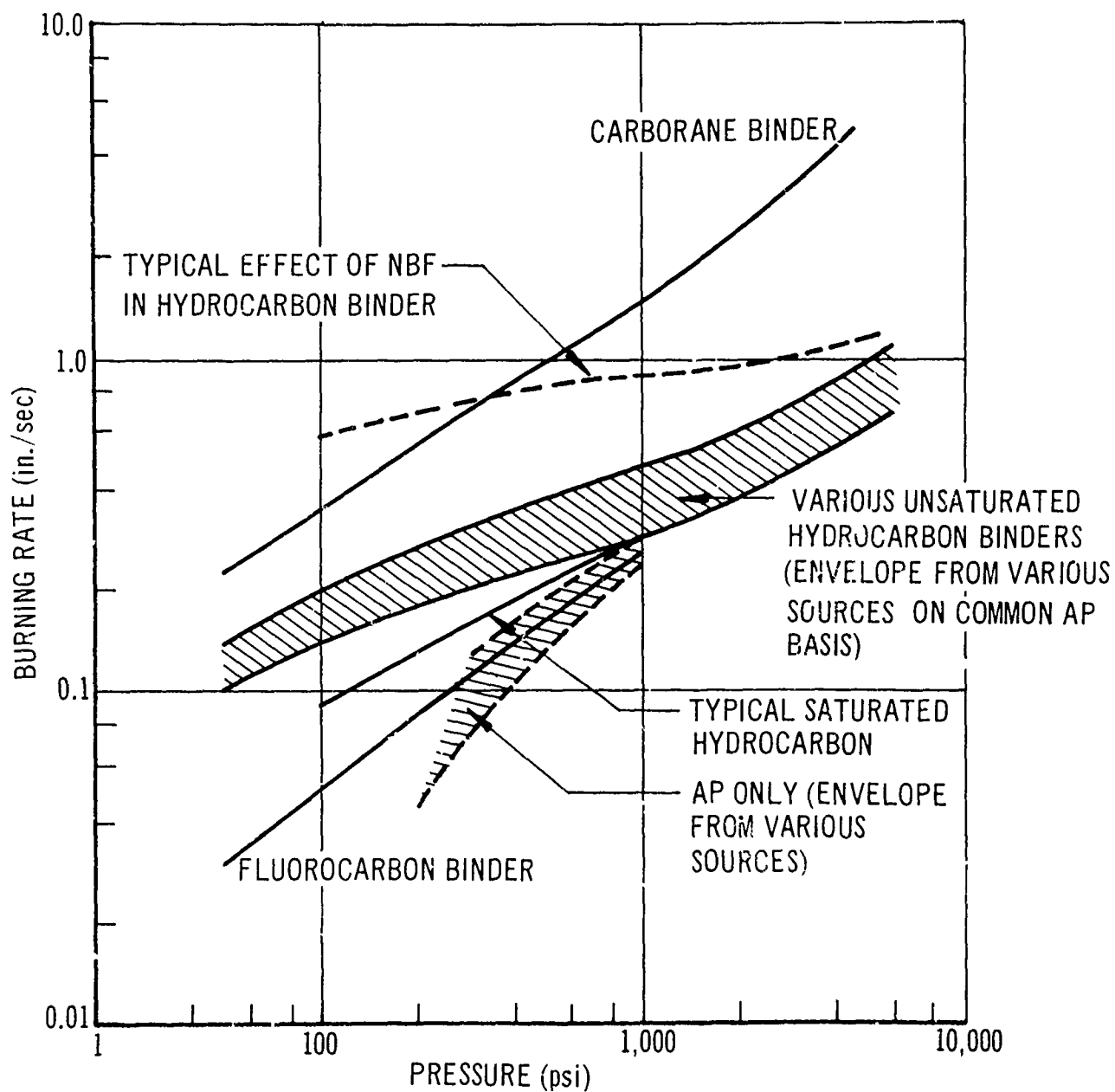


Figure 1 Effects of Inert Binders on Solid Propellant Burning Rate

Effects of varying the type and concentration of plasticizer upon burning rate are minor. Larger, but still secondary, effects are observed when the concentration of plasticizer becomes so extensive that it comprises a major portion of the binder. However, the use of high plasticizer concentration is limited to special developmental purposes not directly associated with combustion.

Aluminum is added to propellants for improved performance and stability. Effects upon burning rate come under the general heading of solids loadings effects and not an effect of the binder per se. Aluminum may be added at the expense of oxidizer (maintaining total solids, lower oxidizer/binder ratio), at the expense of binder (increasing total solids, higher oxidizer/binder ratio) or at the expense of both (increasing total solids with oxidizer/binder ratio decreasing, constant, or increasing). As long as aluminum concentration is not excessive (e.g., within 20 percent), the effect on burning rate is very well correlated to changes in oxidizer/binder ratio (10). This result is in accordance with the form of the combustion model parameter (16) denoting the relative concentrations of oxidizer and binder. Large changes in oxidizer/binder ratio, e.g., from 3.5 to 7.5, can increase burning rate by a factor of 3, but the same result would be predicted merely from increasing oxidizer concentration without consideration of aluminum. In developing a propellant for a specific application, aluminum concentration is generally dictated by other requirements, and adjustments in oxidizer/binder ratio are relatively narrow so that the effect of aluminum is in the secondary area.

In certain situations aluminum per se does influence combustion, but this has been attributed to energy source or sink effects instead of to combustion or binder pyrolysis effects. Thus, aluminum raises the burning rate of low-burn-rate propellants, particularly fine aluminum and at low pressure, but this is attributed to higher flame temperature and radiation (1, 17). The effect is at most moderate, and is mitigated if the aluminum is added at the expense of oxidizer. On the other hand, high aluminum concentrations (greater than 20 percent) reduce burning rate more than would be expected by the associated reduction in oxidizer/binder ratio. Here, extensive aluminum agglomeration inhibits metal combustion and results in a heat-sink effect. Either way, the basic character of the burning rate curve is maintained. Aluminum would appear to play a minor role relative to the effect of binder on burning rate.

b. Moderate Effects

A burning rate effect not large enough to refer to as major, but more than secondary, is observed to result from saturating the hydrocarbon. This was recognized in work reported in Reference 14, and has been more recently applied in propellant work for controllable motors (18). In essence, the moderate effect is an increase in pressure exponent so that the burning rates at low pressure are moderately less than those with unsaturated binders. Polymers used include saturated polyurethane (Estane), polyether diamine (L-2000), and saturated hydroxyl-terminated polybutadiene (Telagen). Unfortunately, these binders did not afford the more classical properties required of a binder. In the absence of funding for further development to

achieve these properties, interest in these binders has waned in favor of most recent approaches to propellant tailoring for controllable motors.

c. Major Effects

Major effects are observed as a result of more radical changes in binder structure, and as a result of incorporating catalysts. Active binders, i. e., binders which themselves are propellants (e. g., double-base, Nitroplastisol, N-F), are beyond the scope of the present program and so are not included in the discussion. However, there are inert binders that do represent a significant change from saturated and unsaturated hydrocarbons.

One inert binder of current interest, representing significant changes in polymer structure and burning rates, is fluorocarbon. The burning rate effect, illustrated in Figure 1, appears to be an exaggeration of the effect of saturating the hydrocarbon. The burning rates are lower, especially at low pressure, and pressure exponent is higher. Also, the burning rates are within the band of data for AP alone, suggesting that the oxidizer controls the burning rate. The reason for this fluorocarbon effect is not known, but it can stem from changes in various combustion model parameters.

Another binder that is receiving increased attention of late is carborane in various forms. Normally considered a burning rate catalyst, as it might well be, recent work has attributed higher burn rates to the rapid kinetics of the AP-carborane reaction (5). This reasoning stems from results of increasing carborane concentration, from additive levels up to a point where the great majority of the binder consists of the carborane leaving just enough CTPB (or other functional polymer) to achieve a cured propellant. Where 70 percent of the binder is carborane, it is difficult to continue to consider the binder CTPB, despite its functional role. Lockheed Propulsion Company, using a carboranesiloxane compound (DEXSIL), has observed a similar effect in Company-sponsored work.

To exploit this trend, consideration is being given to the development of hydrocarbon polymers that would include carboranes in the structure (9). Highly plasticized propellants incur some practical disadvantages. Lockheed Propulsion Company has gone a step further, experimenting with the possibility of polymerizing the carborane so that it truly becomes the binder. Some carborane compounds have functional groups, and success in curing DEXSIL has been achieved. Although cured DEXSIL would not be a practical binder, it is available for representative combustion study. Other functional carborane compounds that would have more practical binder potential could undoubtedly be made given appropriate R&D funds.

The effect of incorporating nBf and similar compounds is well known. It has been attributed to catalysis of reactions involving AP alone and/or to reactions involving AP and binder. The weight of evidence favors the latter hypothesis (1, 19). There is least support for the contention that the effect stems from the binder alone.

The carborane has been regarded as a catalyst when employed in small concentrations; the result shown in Figure 1 can be interpreted as an exaggeration of the effect observed in small concentrations. What is interesting is that the character of the burning rate curve does not change in the same way as with nBf, suggesting a completely different catalytic mechanism or different process (19). The ferrocene exhibits its largest effect at intermediate pressures, causing a reduction in exponent in the vicinity of 1000 psi. The carborane exhibits a larger effect with increasing pressure, causing the appearance of higher exponent over the pressure range of ordinary interest. Their effects on temperature-sensitivity of burning rate are also different (1). Consequently, carborane as an additive as well as an entity is of interest.

2. SELECTED BINDER MATERIALS

The binder materials selected for this program encompass variations that produce a broad range of burning rate effects and representations of a variety of polymer structures. They are either materials used in production propellants, materials that have received considerable developmental usage and test-motor application although not used in current production systems, or materials under consideration for future practical use. The materials are listed in Table I, including curative, plasticizer, and additive typically used with each polymer. Polymer structures are shown in Table II.

Polysulfide has been the subject of propellant combustion research efforts in the past and has been used in production motors. It is representative of a significant change in polymer structure relative to polybutadiene but without a significant difference in burning rate characteristics. The polyurethane and unsaturated polybutadienes may be similarly compared, although there are lesser differences in polymer structure between the unsaturated polybutadienes. PBAN is selected in lieu of PBAA, as a terpolymer previously used in motors.

The Butarez II CTPB binder and the HC-434 CTPB binder are used in current production motors. They differ only in the extent of the polymer chain. Different materials are used to plasticize and cure these polymers.

The HTPB binder is under active consideration for practical use. It varies from CTPB in the end groups (therefore, curative) and in plasticizer. However, the end groups bear a similarity to polyurethane. The burning rate effect is secondary. The HTPB binder is selected in which to perform more extensive variations. This includes the effects of the presence of aluminum and of two different catalysts. Only the catalysts produce major burning rate effects, and the two selected represent different kinds of effects on burning rate versus pressure.

A saturated HTPB, Telagen-S, has been considered for controllable motors because of its moderate effect in increasing pressure exponent (burning rates lower at low pressure). The significant difference is no double-bonds in the polymer.

TABLE I
SELECTED BINDER MATERIALS

Type	Prepolymer	Curative	Plasticizer	Additive ^a
Polybutadienes	R-45	TDI ^b	IDP	---
	R-45	TDI	IDP	Aluminum
	R-45	TDI	IDP	nBf
	R-45	TDI	IDP	DEXSIL carborane
	Telagen-S	TDI	IDP	---
	HC-434	ERL/MAPO	ZL-496	---
	Butarez II	HX-868	Oronite 6	---
	PBAN	Epon 828	DOZ	---
Polyurethane	PPG	TDI	IDP	---
Polysulfide	LP-33	PQD/S	---	Oxides of magnesium and lead
Fluorocarbon	C ₇ FAA	Peroxide	---	---
Carborane	DEXSIL	PAPI	---	---

^a All materials contain 3 percent carbon black for opacity.
A second set of each material contains 10 percent ammonium perchlorate (40 μ), to study effects of AP on pyrolysis yet avoid ignition.

^b Nomenclature

TDI - toluene diisocyanate
IDP - isodecyl pelargonate
ERL - tri epoxide P-amino phenol
MAPO - tris-1-(2-methyl) aziridinyl
phosphene oxide
DOZ - di 2-ethyl hexyl azelate
PQD/S - para-quinome dioxime/sulfur
PAPI - polymethylene polyphenyl
isocyanate

ZL-496 - non-functional
polybutadiene
Oronite 6 - non-functional
polybutadiene
HX-868 - trimesoyl-1-(2-
ethyl) aziridine
Epon 828 - epichlorohydrin -
bisphenol A epoxy
resin

TABLE II
CHEMICAL STRUCTURES OF BINDER PREPOLYMERS

Type	Chemical Name	Typical Structure	N
Polysulfide	Ethyl Formal Polysulfide (LP-33)	$\text{HS}-(\text{C}_2\text{H}_4-\text{O}-\text{CH}_2-\text{O}-\text{C}-\text{H}-\text{S}-\text{S})_N-\text{C}_2\text{H}_4-\text{O}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_4-\text{SH}$	N = 6
Polyurethane	Poly(1, 2-propylene glycol) (PPG)	$\text{HO}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{O}-\left[\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{O}\right]_N-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{OH}$	N = 34-36
Polybutadiene	Polybutadiene-acrylic acid - acrylonitrile terpolymer (PBAN)	$\left[\underset{\text{CH}_2}{\text{CH}} = \underset{\text{CH}_2-\text{CN}}{\text{CH}}-\underset{\text{CH}_2-\text{COOH}}{\text{CH}}-\text{CH}_2 \right]_N$	N = 15-17
Polybutadiene	Carboxyl terminated polybutadiene (Butarez II)	$\text{HOOC}-\left[\text{CH}_2\text{CH} = \text{CHCH}_2\right]_N-\text{COOH}$	N = 95-100
Polybutadiene	Carboxyl terminated polybutadiene (HC-434)	$\text{HOOC}-\left[\text{CH}_2\text{CH} = \text{CHCH}_2\right]_N-\text{COOH}$	N = 30-35
Polybutadiene	Hydroxyl terminated polybutadiene (R-45)	$\text{HO}-\left[\text{CH}_2\text{CH} = \text{CHCH}_2\right]_N-\text{OH}$	N = 40-50
Polybutadiene	Saturated hydroxyl terminated polybutadiene (Telagen-S)	$\text{HO}-\left[\text{CH}_2\text{CH}-\text{CHCH}_2\right]_N-\text{OH}$	N = 95-100
Fluorocarbon	C ₇ fluoroalkylacrylate	$\text{H}(\text{CF}_2-\text{CF}_2)_3-\text{CH}_2\text{OOCCH} = \text{CH}_2$	
Carborane	Polycarboranesiloxane (Dexsil 202)	$\text{HO}-\left[\underset{\text{CH}_3}{\text{Si}}-\underset{\text{C}_6\text{H}_5}{\text{C}}-\underset{\text{CH}_3}{\text{Si}}-\underset{\text{C}_6\text{H}_5}{\text{C}}-\text{O}-\underset{\text{CH}_3}{\text{Si}}-\underset{\text{C}_6\text{H}_5}{\text{C}}-\text{O}-\underset{\text{CH}_3}{\text{Si}}-\underset{\text{C}_6\text{H}_5}{\text{C}}-\text{OH}\right]_N$	N = 4-5

A significant change in polymer structure and resultant burning rate curve exists with fluorocarbon, under more active consideration for controllable motor and high density-impulse propellants.

Finally, a carborane binder, representing what is thought of as a catalyst as the material constituting the complete binder itself, must be considered. It goes far beyond the objective of Reference 9 from a combustion standpoint, but is, however, appropriate for this combustion research program. It is sufficient that LPC has succeeded in curing DEXSIL carborane, actually a polycarboranesiloxane; that DEXSIL may not itself be a practical binder does not preclude interest in carborane binders. The polymer structure is considerably different from polybutadiene, and the burning rate effect is major.

SECTION IV

EXPERIMENTAL METHODS

1. PREVIOUS EXPERIMENTAL STUDIES OF BINDER

a. Low Heating Rate Methods

Although the mechanisms of pyrolysis, oxidation, and burning of polymeric materials have been actively researched in the past, little attention has been given to the study of practical binders used in solid propellants. Furthermore, in the majority of such research programs, the emphasis is placed on "bulk heating" techniques (namely, differential scanning calorimetry and thermogravimetric analysis), which provide data at heating rates several orders of magnitude less than that imposed on a binder in solid propellant combustion (10). To dismiss these programs as irrelevant to the task of understanding the role of binders in solid propellant combustion would be incorrect. At the same time, however, to rely on existing data from bulk heating techniques for practical binders would deny that binder pyrolysis, oxidation, and burning are dependent upon heating rate.

b. Experimental Approaches Employed in Linear Pyrolysis Studies at High Heating Rates

In the first attempt to measure the linear pyrolysis rate of a polymeric material at propellant combustion heat rates, the hot-plate technique was employed (20,21). In this technique, the test sample is forced against a flat, heated plate that provides thermal energy representative of propellant combustion. The linear pyrolysis rate is measured from the rate of the change of the sample position, and the temperature is measured with a thermocouple interposed between the sample and the heated surface.

Although this instrument provides an excellent means to characterize the pyrolysis of a large number of materials, it was found that certain materials cannot be studied. Specifically, materials that leave solid residue during pyrolysis (namely, binders) yield unsatisfactory test results. Additional criticism has been leveled at this test approach by Nachbar and Williams (22). This criticism was based on the fact that products of decomposition have no path of escape from the hot plate other than along the interface surface. This condition results in a thin layer of gases between the test sample and the thermocouple, which could produce an appreciable error in temperature measurement. To correct this situation, Nachbar and Williams employed a porous hot plate. Whereas this modification proved satisfactory for materials that did not produce a residue during decomposition, it has proved unsatisfactory for residue-forming materials (most practical binders) because the hot plate loads up during a test (23). Coates (24) reported successful test results using a noncharring wax in a porous hot-plate pyrolysis apparatus. Based on this previous experience, the hot-plate technique is deemed inappropriate for binder pyrolysis studies.

A second technique for studying binder decomposition at heating rates comparable to those encountered in propellant combustion uses a radiation heat source. Basically, the binder sample is exposed to controlled levels of radiant energy and the linear pyrolysis rate is inferred through sample weight loss. One important aspect of this technique is that the radiative source is used to simulate the thermal-conductive flame-source that predominates in solid propellant combustion. For radiative sources to provide an acceptable simulation of this heat transfer process, the optical absorption depth in the polymer sample must be negligibly small compared to the preheat zone thickness in the solid.

Shannon (25) has conducted binder pyrolysis tests using a radiant energy source consisting of 11 quartz lamps of 500 watts each. To prevent in-depth absorption of radiant energy, each binder was formulated with 3- to 4-percent carbon black. Exposure of binder by a CO₂ gas laser presents an alternative to filling the binder with an inert pacifier. Friedman (26) et al have observed that the absorptivity of polymetric materials is such that binders are essentially opaque to the 10.6-micron wavelength emitted by the laser. However, the CO₂ laser is relatively new to solid propellant combustion research and, as a result, it has not achieved the standardized usage of other radiative sources (e.g., carbon and xenon arc furnaces).

The radiation technique provides several advantages over other techniques. First, it is possible to subject the test sample to different environments without altering the energy supplied to the decomposing surface. This, of course, presumes that a reactive environment does not enter into a vigorous decomposition process that provides appreciable heat generation. Second, the sample is free of mechanical devices or combustion flames that could mask the surface so that visual observations or high-speed motion picture studies are complicated. Finally, the radiation technique provides a relatively economical means of providing a controlled level of energy to the binder surface.

Several disadvantages to a radiation technique are worthy of mention. First, the products of pyrolysis tend to attenuate radiation arriving in the vicinity of the binder and, in effect, negate the validity of calibrations that are made when the binder sample is not present. Removal of products of pyrolysis by a purge presents one method of reducing this error. Second, the calibration for the radiation furnace is expressed as the incident energy on the test sample. If an appreciable amount of energy is reflected off of the surface, the validity of the calibration is again negated. This shortcoming is removed by the incorporation of an opacifier in the binder, as described previously.

The third approach that has been used in the past in studying binder pyrolysis deals with convective heating of binders. This can be accomplished by directing a heated gas at the binder surface or by establishing combustion between the pyrolyzed vapors above the binder surface (self-heating). In both techniques, the primary modes of heat transfer are convective and conductive rather than radiative; thus, the thermal environment of actual combustion is simulated. McAlevy (27-29) has employed the technique of self-heating to the study of a number of binders and has

discovered several disadvantages to this method of testing. First, the range of heat flux levels in a self-heating method is limited; specifically, heat flux levels are dependent upon flammability limits of the particular systems studied, while other techniques, such as radiative heating, have limits depending upon the ultimate output of the heating apparatus. Second, the surface pyrolysis characteristics of many polymeric materials cannot be investigated with self-heating. This results because of the inability to ignite some materials, and, where burning is possible at selected oxidizer flow rates, the flammability limits are such that both low and high heat flux levels are impossible.

Other problems pertain to knowledge and control of the heat flux delivered to the binder surface. Essentially, there is no method to measure heat flux during a test. Thus, this important parameter must be calculated. Because such a computation is based upon the flame temperature, standoff distance of the flame, thermal conductivity of the products of binder pyrolysis, and blowing effects at the binder surface, results are subject to considerable error. In fact, the complexities of modeling this flow field approach those of modeling solid propellant combustion. Thus, accurate calculation of heat of pyrolysis is precluded.

Another problem associated with heat flux is controlling the level during a test. Movement of the binder surface to keep it stationary while undergoing pyrolysis has been attempted by McAlevy. However, because the diffusion flame typically resides in close proximity to the binder surface, small changes in binder position relative to the flame location can lead to large changes in heat flux arriving at the binder surface.

Finally, the method of convective or self-heating does not lend itself to studying the influence of different environments in a controlled manner. The major problem is that the mixing and counter diffusional processes between oxidizing environment and pyrolysis products cannot be represented without relying upon simplified analysis of the flow field, which could lead to erroneous test interpretations.

c. Results of Previous Binder Pyrolysis Studies

It is instructional to consider typical results of binder studies for the purpose of revealing the poor understanding of binder pyrolysis. Although McAlevy's work, apart from the uncertainties involved, would appear to have been among the more relevant regarding simulation of combustion conditions, and modeling needs, his work has not emphasized practical binders. His most recent work has been with polymethylmethacrylates, polypropylene, polystyrene, nylon, and delrin. His work with the convective heating technique has provided information concerning the possible role of oxidative environments that must be considered.

Perhaps the most extensive study of the role of perchloric acid on binder decomposition and propellant combustion is contained in the series of papers co-authored by Pearson (30-33). A summary discussion is contained in the literature survey (10). Results of these studies certainly prove that perchloric acid or a chlorine oxide decomposition product is a powerful

reagent for heterogeneous reaction, more so for some polymers than others. However, these studies do not include kinetics or energetics data. It was not the intent to acquire such data, and the method of exposing the sample to perchlorate acid was too qualitative for such purpose. Sandwich studies (34-36) have shown that AP and binder do not react interfacially, at the contact face, but do not preclude heterogeneous reactions in a propellant.

Schmidt began work involving the effects of binder components on propellant strand burning rates (37). His initial conclusion was to distinguish between fuels that char and fuels that melt and volatilize without residue. However, the work was limited at the time, did not use practical propellant compositions, emphasized the oxidizer according to the older Shannon theory of ignition front propagation, and was pointed toward extracting simplified mechanistic criteria rather than combustion analysis. His more recent work has been concerned with how fuel components might be able to affect AP processes rather than with binders as such (38).

The work of Shannon (25) represents the most useful contribution to improving the understanding of the binder in solid propellant combustion. In that research program, the thermal decomposition characteristics of four binders (PBAN, PU, CTPB, and CTPIB) were studied using DSC and radiant exposure techniques. Shannon concluded that the thermal decomposition mechanism of polymer materials changes with the heat rate. Hence, the DSC tests are of little value if propellant combustion conditions are of interest. Shannon took preliminary steps to establish heat of pyrolysis for each of the binders. However, test data were not adequate to obtain this parameter or kinetics. Nevertheless, the radiant heating approach to studying binder pyrolysis appears sound and worthy of a more intensified and systematic study of practical binders.

In summary, it is evident that meaningful studies of binder pyrolysis/decomposition have been hampered in the past by inadequate test methods. Much of the existing data are suspect in their applicability to propellant combustion and, therefore, to use in combustion analysis and combustion tailoring study. Attention must be given to preventing these problems by revealing valid measurement techniques before embarking on extensive tests, and testing should be performed with practical binder materials.

2. PYROLYSIS EXPERIMENTS

a. The Arc Image Furnace Method

Data relative to mass loss and surface temperature were obtained by means of the LPC xenon arc image furnace in conjunction with a narrow-band infrared pyrometer. It is recognized that the use of radiant energy has some disadvantages. However, if proper consideration is given to evaluation of data, the arc image technique provides an excellent approach to pyrolysis studies. The capabilities and limitations of the technique are well established by virtue of its extensive use in ignition studies. The technique permits testing over a wide range of calibrated flux levels (5 to 300 cal/cm²-sec) at predetermined, controlled time increments. The arc image system is equipped with a test chamber that provides the means to examine

the effect of different environments in an effective and uncomplicated manner. Additionally, the window in the test chamber, which is used to transmit the radiant energy to the test specimen, provides the capability for photographing the sample surface during exposure to the energy. It is also possible to view the surface with an infrared pyrometer, to determine sample surface temperature, without interfering with either the sample surface or the environment. However, there are certain problems that must be dealt with if the data are to be meaningful.

First, the use of radiant energy to decompose the binder creates a heating condition that is not representative of the primary mode of heat transfer in solid propellant combustion. In a recent study (39), the ignition characteristics of relatively transparent propellant (CTPB/AP), propellant containing an opacifier (CTPB/AP/carbon black), and propellant having a nonreactive coating of opaque material (zirconium carbide, or tungsten carbide) were examined. Results showed a significant difference in ignition energy requirements for the three configurations. The presence of the carbon black opacifier reduced the energy required for ignition by a factor of about 2. In any test utilizing a radiative source, it must be recognized that some in-depth heating will occur, thereby creating thermal wave conditions different from that present in propellant combustion. The incorporation of an opacifier in the specimen represents one solution. As described previously, this approach was also used by Shannon (25) in his binder pyrolysis study. This permits the energy to be absorbed at the surface, and the interior of the sample is heated by thermal conduction.

A second aspect that required consideration in this program was related to the movement of the sample surface in the source focal volume as the specimen pyrolyzes. The size of the focal volume is regulated by the spacing of the electrodes in the source lamp. Initially, the test specimen is located at the exact focal point, as determined by mapping the focal volume with a calorimeter. Such mapping reveals that the flux decays significantly as the calorimeter is moved out of this focal volume. In order to maintain a constant flux at the sample surface, it is necessary to either ensure that the sample does not recede out of the focal volume, or to program current to the lamp to increase the flux at the edges of the focal volume as the sample recedes. Since the latter approach would require elaborate modification to the electronic system, it was elected to maintain the sample within the focal volume by placing an upper limit on exposure time depending upon regression rate.

One other area where the problem of flux attenuation can cause a problem is associated with the deposit of decomposition products or smoke on the quartz window through which the radiant energy is delivered to the test specimen. This was corrected by sweeping the pyrolysis products away from the window with the environmental gas. Since the window could be inspected for residue, or motion pictures taken, the success of the purging method could be verified. These pyrolysis products still create a certain amount of flux attenuation above the sample surface. However, this is true regardless of the heating source employed to pyrolyze the binder. Movies taken during this program indicate that the degree of such attenuation is principally a function of heat flux. Since data were taken at several time

exposures, it was possible to ascertain an equilibrium period before the attenuation became excessive. Moreover, since the infrared pyrometer used is sensitive to a narrow spectral region, the attenuation did not affect surface temperature measurements; the principal effect was upon use of the results in an energy balance equation.

In evaluating the advantages and disadvantages associated with the use of the arc image technique for pyrolysis studies, it appears that more reliable data can be obtained by this method than by other methods available at this time.

b. The LPC Xenon Arc Furnace System

The LPC arc image system utilizes a 20 kw xenon lamp in conjunction with opposing dual ellipsoids/mirrors in the configuration shown in Figure 2. Exposure time is controlled by means of a fast-response shutter system located at the optical crossover point between the two mirrors. The shutter is controlled by an electronic programmer/timer (Hill Enterprises, Model NOTS-603, Ridgecrest, California), which provides exposure times from one millisecond to 10 seconds. An overall view is shown in Figure 3.

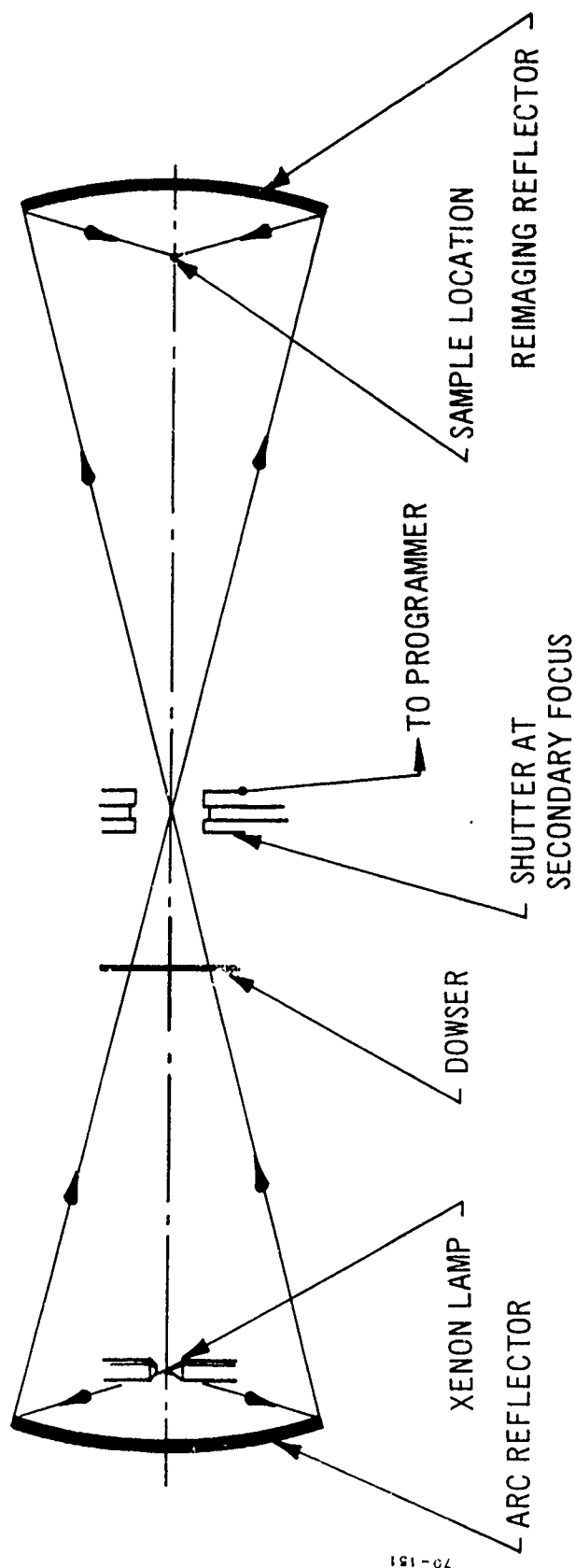
The system is equipped with a test chamber having a 3-inch quartz window for transmission of the radiant energy. The chamber, shown schematically in Figure 4, can be pressurized or evacuated and is designed to permit purging to eliminate deposit of decomposition products on the transmission window. The chamber is mounted on a micrometer stage to permit location of the test specimen at the exact focal point of the secondary mirror. A gas sampling valve is mounted on the chamber to permit samples of the decomposition products to be taken for gas chromatographic or mass spectrographic evaluation. The chamber is shown in position in Figure 5.

The test specimen is retained in a glass ring and mounted in a stainless steel plug that forms the base of a purged duct when installed in the test chamber. These are shown in Figure 6.

A 2-inch hole in the center of the secondary mirror (in line with the test specimen) permits the specimen to be viewed by either a high-speed camera or a temperature recording device without interrupting the path of the radiation energy. The radiometer in place is shown in Figure 7.

Heat flux is measured by water-cooled asymptotic calorimeters (Hy-Cal Engineering, Sante Fe Springs, California) placed at the focal point which is normally occupied by the binder sample. Three calorimeters are used for recording over the range of 5 to 300 cal/cm²-sec. Each calorimeter was recalibrated by the manufacturer at the beginning of this program.

Flux level is controlled by varying current to the xenon lamp and by use of calibrated sets of wire mesh screens for fine flux adjustment. Calibrations are made before and after each set of data has been taken. Before the pyrolysis program was started, a series of calibrations was made



70-151

Figure 2 Arc Image Furnace Optical Arrangement

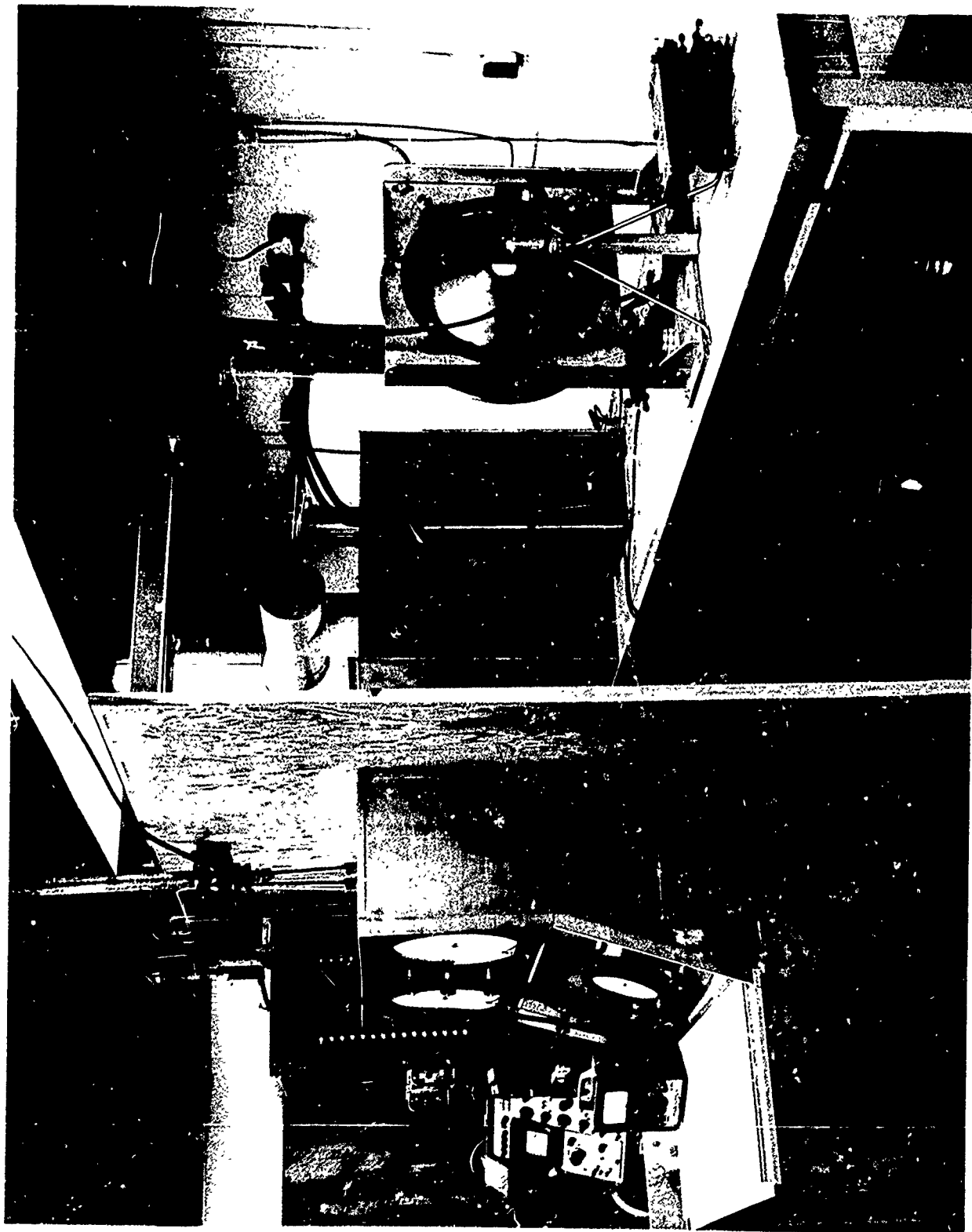


Figure 3 LPC Xenon Arc Furnace Apparatus

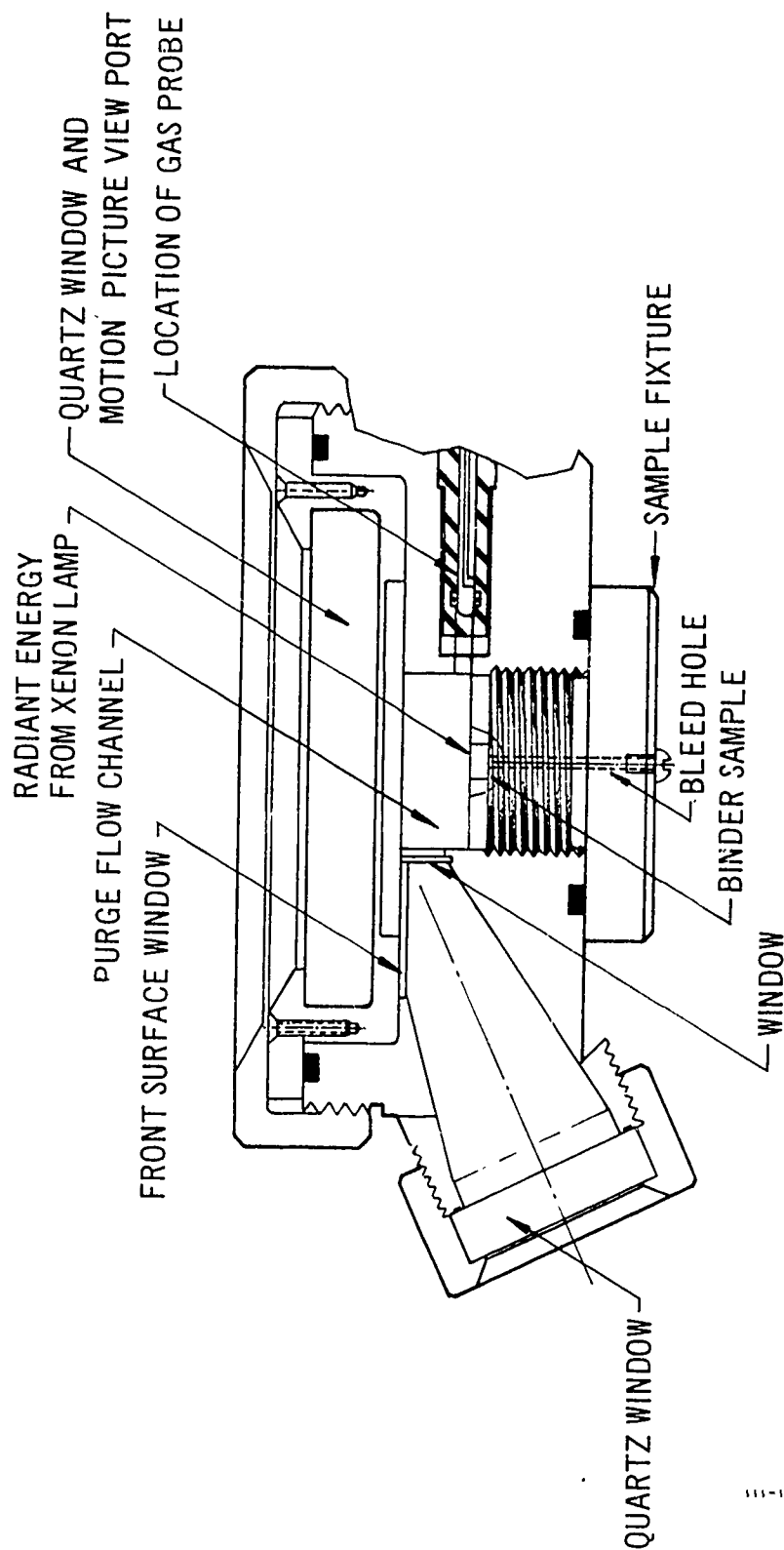


Figure 4 Schematic of Xenon Furnace Test Chamber

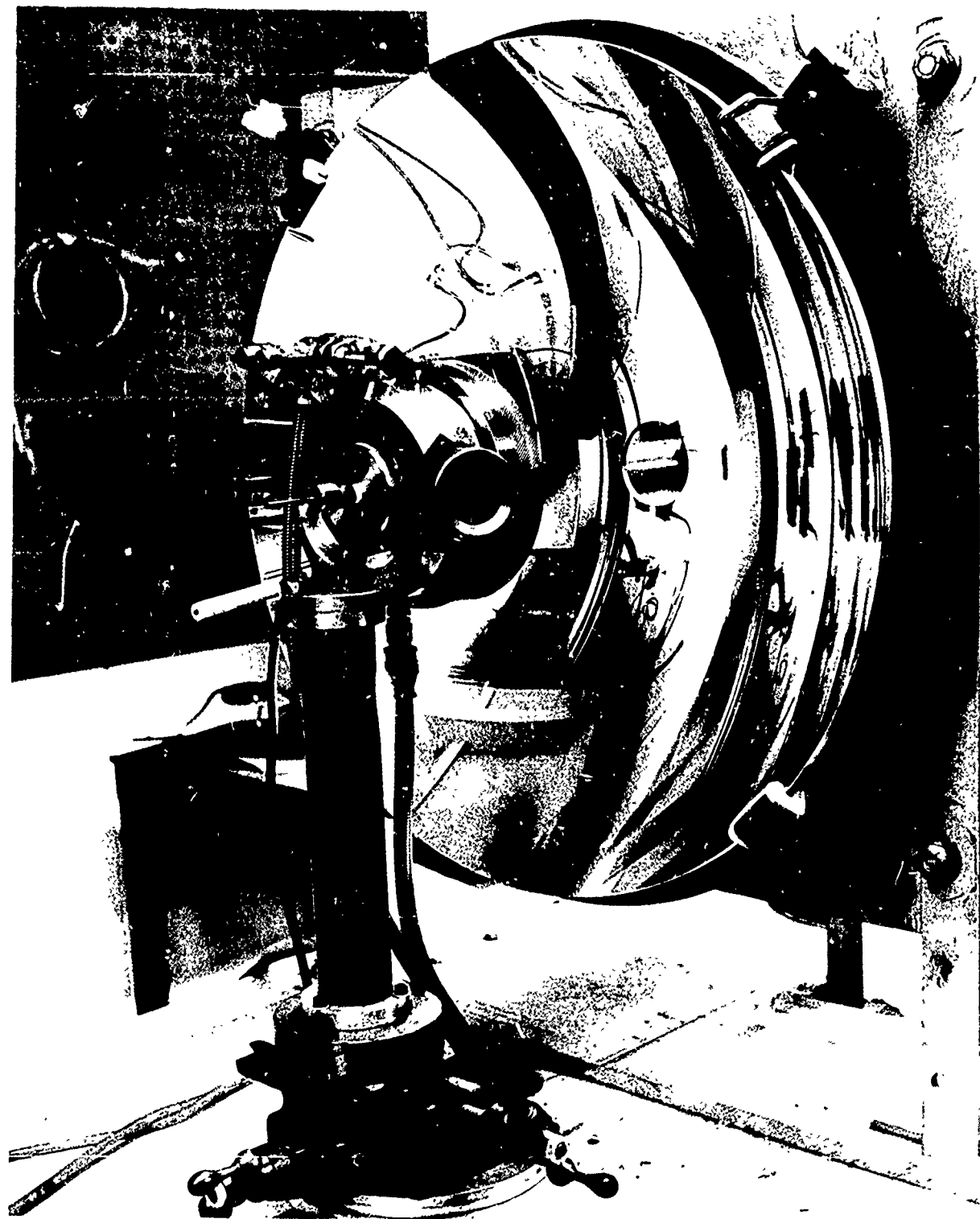


Figure 5 Combustion Chamber for Xenon Arc Furnace

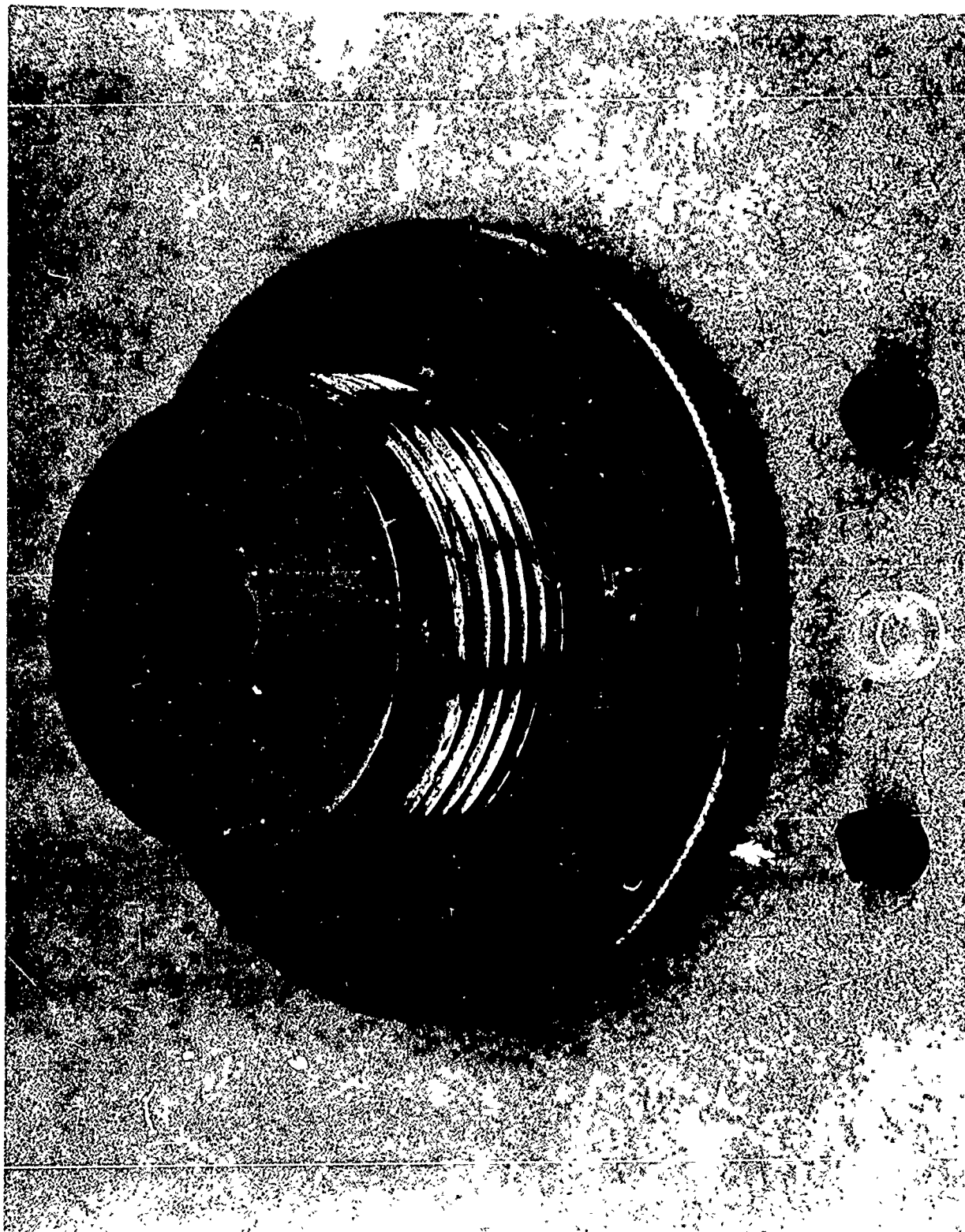


Figure 6 Test Specimen and Holder

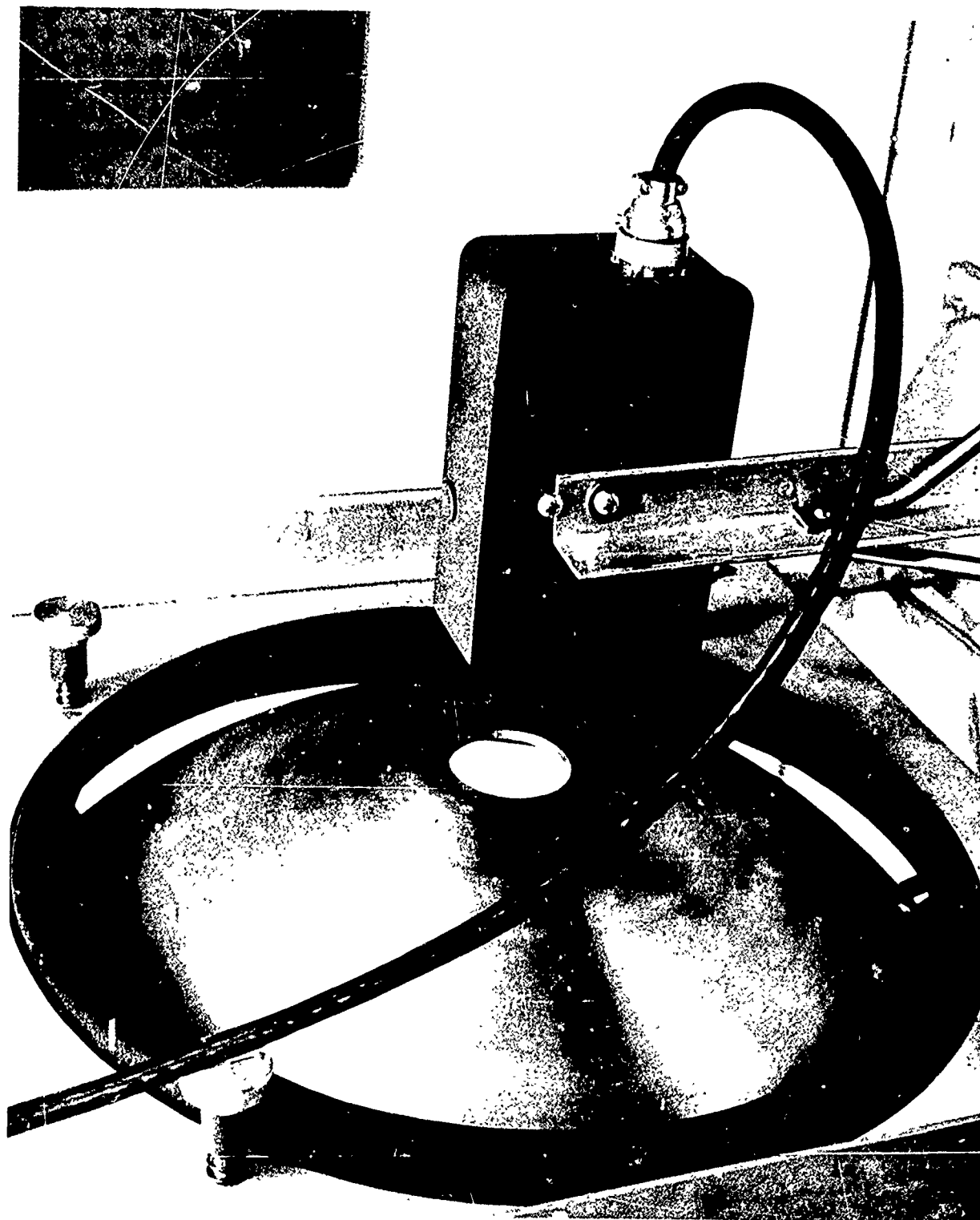


Figure 7 Radiometer in Place Behind Reimaging Reflector

to determine flux variations over 8-hour periods. Results indicated a variation of 1.4 percent at a given flux level if no adjustment to lamp current was made. In practice, a calibration is made before test, and current adjustment is made as required.

c. Surface Temperature Instrumentation

Surface temperature measurements are made by means of a Model TD-6 pyrometer, manufactured by Infrared Industries, Santa Barbara, California. The pyrometer records temperatures over the range of 420 to 3900°C. A schematic of the optical system is shown in Figure 8. The TD-6 lead sulfide detector with dichroic mirror filter is sensitive to wave lengths between 1.6 and 2.7 microns. Since the xenon lamp peaks at 0.8 to 1 micron, the instrument is ideally suited for use with the arc image furnace. The TD-6 has a reported accuracy of ± 2 percent of recorded temperature, and a response time of 30 milliseconds. Output is recorded by meter for visual observation, and on a Tecktronics Model 549 permanent record oscilloscope. The pyrometer was calibrated by the manufacturer against a black body source.

One area of concern in temperature measurements of this type is the emissivity of the material under observation. The emissivity of the binders was unknown, but the addition of 3-percent carbon black ($\epsilon = 0.92$) helps provide a more uniform emissivity. Consultation with the manufacturer resulted in the selection of $\epsilon = 0.89$ for the pyrolysis study. It is recognized that this is an arbitrary value. However, emissivity will change somewhat during binder decomposition, and this could introduce some error in recorded temperature even if the initial emissivity were known precisely. A grasp of the possible error in reported temperatures may be obtained by the following approach.

The temperature calibration of the Model TD-6 is approximately of the form

$$S = kT^5$$

and the signal S obtained from a source of emissivity ϵ is given by

$$S = \epsilon kT^5$$

In the event an erroneous emissivity (ϵ') is employed in the slide rule temperature calculation, the resulting temperature will differ from the true temperature. The relationship between the calculated temperature (T') and the true temperature (T) is approximately

$$T' = \left(\frac{\epsilon}{\epsilon'} \right)^{1/5} T$$

For small errors in emissivity the percentage error in temperature will be approximately one-fifth the percentage error in emissivity.

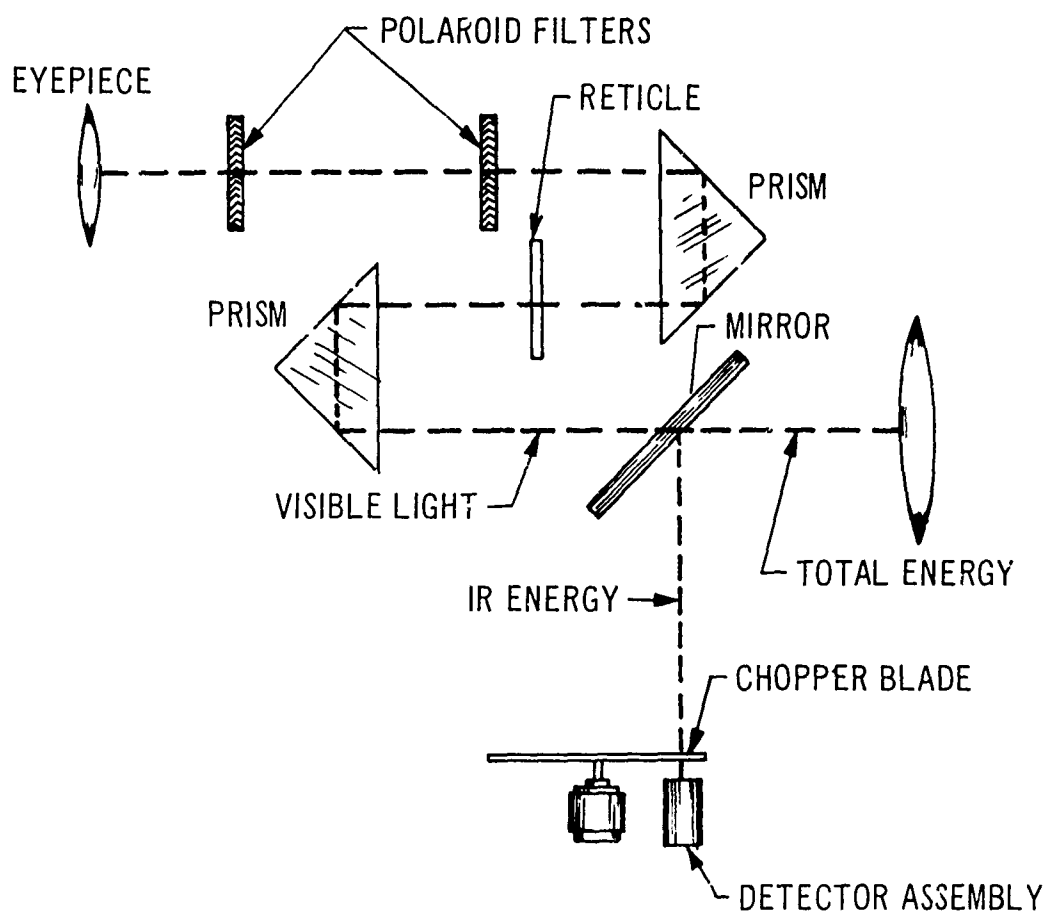


Figure 8 Optical System Schematic

The magnitude of the temperature error introduced by an error in emittance depends on the spectral range of the radiation parameter and the temperature of the target. The manufacturer has determined for the TD-6 used in this program that the following comparisons are valid for a 10-percent error in emissivity:

<u>True Temperature ($^{\circ}\text{F}$)</u>	<u>Recorded Temperature ($^{\circ}\text{F}$)</u>
200	196
500	491
1000	980
2000	1945
4000	3830

In the table of emittance values for various materials, asphalt, tar, and rubber are listed as having an emittance of 0.95. Since these materials are somewhat similar in opacity and consistency to the binders with carbon added, it would appear that the selection of an emittance value of 0.89 is not unrealistic. The possible difference between true temperature and recorded temperature is therefore small in the temperature ranges recorded in this program.

The optical system of the pyrometer is such that the 0.125-inch-diameter sample completely fills the reticle to provide a temperature measurement averaged over the entire surface of the sample.

d. High-Pressure Specimen Chambers

The optical arrangement of the arc furnace system is such that the energy can be transmitted through a 3-inch-diameter quartz window. Quartz of $\frac{1}{2}$ -inch thickness permits flux levels up to 300 cal/cm²-sec to be achieved. However, the highest pressure that the window can sustain is approximately 300 psi. Since data were desired in the 1000-psi regime at maximum flux, the chamber was modified to increase the pressure capability without sacrifice in energy flux delivery capability. The modification utilized a Lucite window in a dome configuration, Figure 9, which transmits the energy radially.

The high-pressure chamber with dome window met the high-pressure, high-flux requirements. Repetitive tests revealed no difference in mass loss data, for a given flux and pressure, as between the two chambers. However, problems were encountered in obtaining surface temperature data through the Lucite.

No problems were encountered during the portion of the program involving pressures at or below 250 psia. For these tests, the standard chamber configuration with the quartz window was used. However, when the high-pressure Lucite window was installed, it was discovered during checkout that the TD-6 pyrometer was not "seeing" the temperature through the Lucite. Consultation with the manufacturer resulted in an evaluation of the Lucite dome window by Infrared Industries, who then

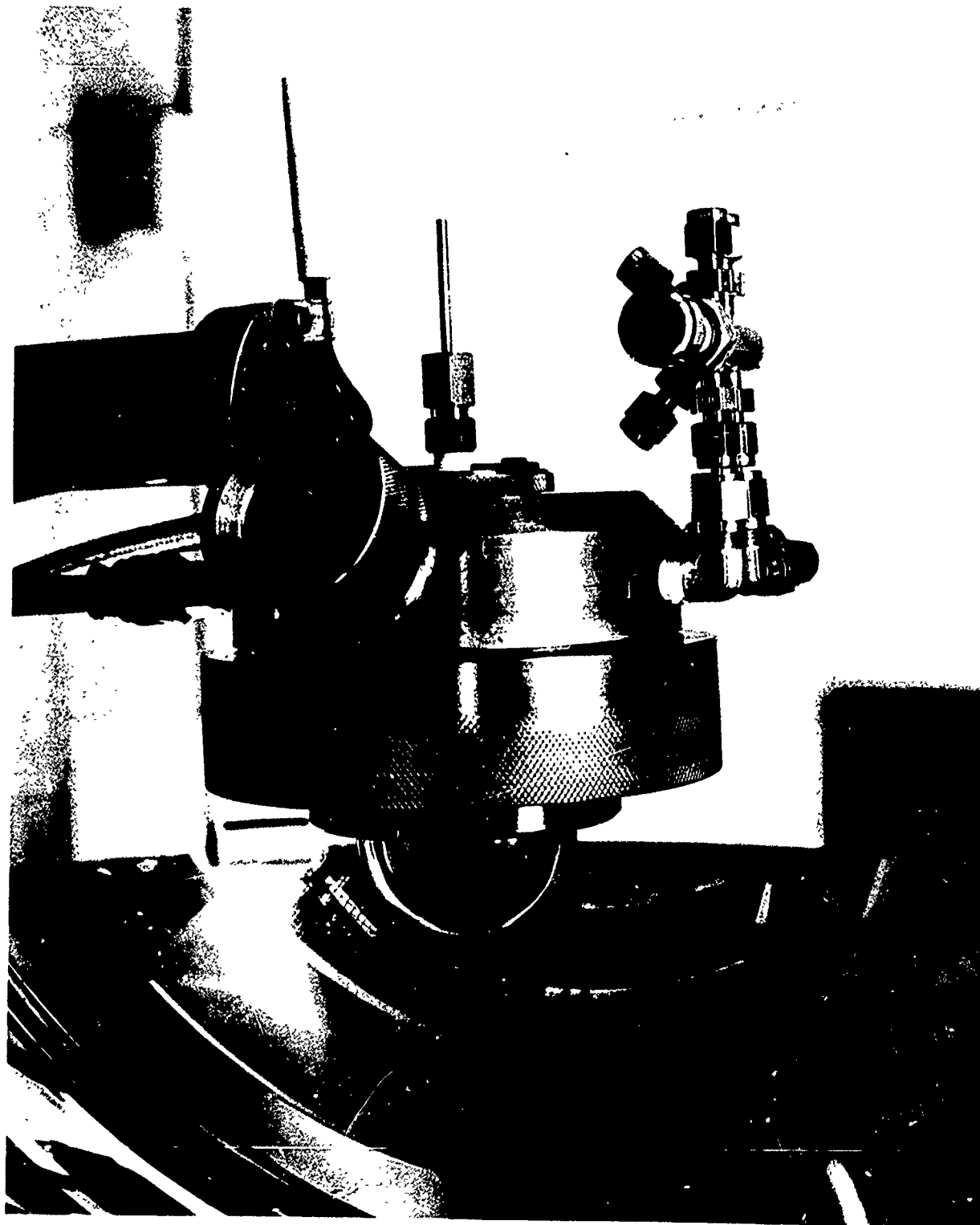


Figure 9 High-Pressure Lucite Dome Test Chamber

recommended an instrument, Model TD-9, modified to produce satisfactory temperature measurements through the Lucite window. Calibrations were made through the window at the factory using a black body source. However, when the TD-9 was used in conjunction with the arc image furnace, it was found that the TD-9, which could record the temperature through the Lucite, was sensitive in the same wavelength at which the xenon lamp peaks: 0.8 micron. Consequently, the reflected energy from the source matched perfectly the transmission characteristics of the window and the sensing cell. Neither Infrared Industries nor LPC could find an immediate, practical solution to measurements that would be compatible with both the Lucite and the arc source.

Subsequently, the standard low-pressure configuration was modified by reducing the aperture and increasing the window thickness. This resulted in drastically reducing the flux delivery capability at 1000-psi test pressure. Consequently, only mass loss data were obtained at the high-flux, high-pressure combination in the Lucite dome, but both mass loss and surface temperature data were obtained at 50 cal/cm²-sec and 1000 psi.

e. High-Speed Movies

High-speed movies were made of binders during exposure to the radiant energy using a Hy-Cam 16mm camera with a 135mm Soligor lens. The camera was mounted in the same location used for the pyrometer for surface temperature measurements. Type III Kodachrome film was used. The framing rate and aperture were varied for different flux levels and exposure times.

Problems were encountered under some flux/pressure conditions due to smoke above the surface of the specimen. Increasing the purge did not always correct the problem. However, surface processes (melting, boiling, char formation) were recorded before the smoke became sufficiently dense to obscure them. Because of the large number of binders and conditions under study, it was not possible to optimize film quality for each condition. The best quality movies were generally obtained at lower heat flux.

f. Gas Sampling

Gas samples were obtained by means of a Loenco Model L-208-6 valve, shown in Figure 10. The valve was mounted on the test chamber, as shown in Figure 5; a closer view is in Figure 9.

Before a test, the cleaned valve is attached to the chamber connectors with the plunger in the withdrawn position. The valve remains open during the exposure and is closed immediately after the shutter closes. The valve is then disconnected from the test chamber and delivered to the analytical laboratory. Exposure time was adjusted to provide sufficient sample for analysis.

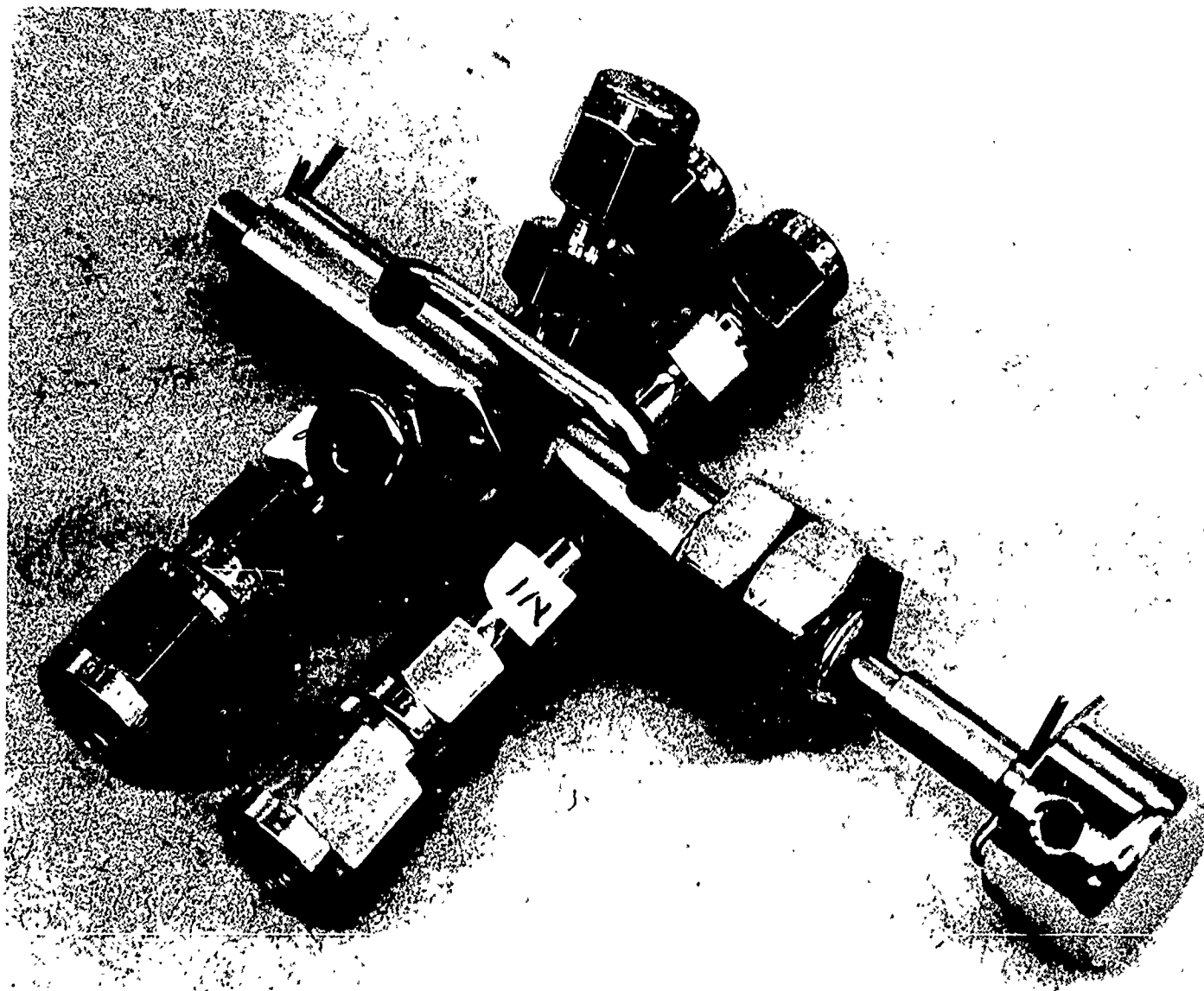


Figure 10 Loenco Gas Sampling Valve

g. Oxidative Atmospheres

A series of tests was conducted with chlorine as the environmental gas. The system was maintained as used for tests with nitrogen. No changes in the test apparatus were necessary, except for a vacuum line to maintain subatmospheric test pressures to avoid gas phase reactions. Subatmospheric test pressures were similarly used in limited testing with air as the environmental gas.

h. Test Specimen Preparation

Bulk samples of the binders were cast in quart milk cartons. Individual arc image test specimens were taken from slices cut from the bulk sample.

Consistency and texture of the binders differed greatly because of lack of solids loading. Difficulty was experienced in handling some of the binders. Because of these variations in consistency, several techniques were explored in order to obtain uniform test specimens. CTPB and HTPB were the easiest of all binders to handle. Polyurethane, fluorocarbon, and polysulfide presented the greatest problems. For those binders that could not be sliced at room temperature, the bulk sample was frozen to facilitate slicing. Test specimens were cut from the slices by means of a letter punch where possible. Special cutters were fabricated in an attempt to avoid the characteristic hour-glass shape that results when rubbery material is cut. With all precautions, this tendency continued. A solution was found by cutting thicker samples of larger-than-required diameter, and then cutting out the hour-glass center section. After the specimen was installed in the glass retaining ring, the samples were allowed to relax and were subsequently trimmed to provide a uniform surface. Samples from softer binders were prepared by forcing the binder through the ring, allowing it to relax and smoothing the surface. Some minute voids were unavoidable with some binders. It appears that the total absence of AP has some effect upon the curing process.

During the acquisition of baseline data for CTPB and HTPB, a series of samples was weighed to determine weight uniformity. Sets of 10 specimens were cut, placed in retaining rings, and weighed to the nearest 0.1 milligram. Average weight and standard deviation were determined. Results from four sets of 10 indicated standard deviations ranging from 3.3 to 4.0 percent for CTPB and from 5.0 to 5.9 percent for HTPB. While some binders exhibited larger deviations due to difficulty in handling, the maximum deviation was 8.5 percent in a 10-sample set of polysulfide.

Glass retaining rings were used to reduce heat loss. Samples were cut to 0.125 inch in diameter by 0.250 inch in length.

During the initial portion of the program, sufficient tests were repeated to determine reproducibility of data. In the process of reproducibility testing with CTPB, it was discovered that there was a difference in both mass loss and temperature measurements when samples were taken from different slices of binder. Investigation revealed that

slices used in the first tests had come from the bottom of the milk carton into which the CTPB had been cast. It appeared that the carbon black had settled out, becoming of sufficient concentration to affect the data. Subsequently, specimens were cut from sequential slices in a described pattern until a section was reached where uniform data could be obtained. Original data were discarded. All tests thereafter were conducted with samples from several slices taken from the middle of the bulk sample before the test sequence was started. In all tests, samples were taken from random locations across the slice so that data would not represent a preferred location.

i. Mass Loss/Surface Temperature Data Acquisition

At the beginning of the program, a series of tests was conducted to determine the minimum number of samples to be tested for each datum point. Although the program involved a large number of binders, with and without AP, which were to be examined over a wide range of conditions, once the experiment is set it can proceed rapidly with repeat samples. Results of exploratory tests revealed that reliable data could be obtained by use of five specimens per datum point. However, if a large dispersion was noted within the five samples, additional samples were tested to determine the validity of the data. Data were reduced to the numerical average of five mass loss and temperature measurements. Standard deviation was determined by the range method:

$$\sigma = rk$$

where

r = difference between maximum and minimum value within the set

k = constant for a specific number of test points

σ = standard deviation

Mass loss was determined by weighing the specimen, to the nearest 0.1 milligram, before and after exposure to the radiation. Post-test measurements were made with surface residue removed. Several techniques were used to remove the residue layer, depending on the characteristics of the material. If the residue was in the form of powder, it was brushed off lightly with a fine brush. If it was a solid char, it was lifted off with the edge of a razor blade. When the residue was viscous, a tiny swab made of lens tissue was carefully rolled across the surface. Samples were examined microscopically to ensure that no extraneous material was left on the surface prior to weighing.

Temperature measurements were made from oscilloscope traces of the output of the infrared pyrometer previously described. The traces are a record of millivolt output versus exposure time. An example is shown in Figure 11. Measurements were made at several points across the flat portion of the curve to arrive at an average temperature. These readings were converted from millivolts to temperature from a table supplied by the manufacturer.

PRESSURE - 15 psia N₂

FLUX - 35 cal/cm²-sec

TIME - 1 sec

5 mv/cm

200 ms/cm

Av T_s - 670°C THIS TEST

665

670

665

675

REPEAT TESTS

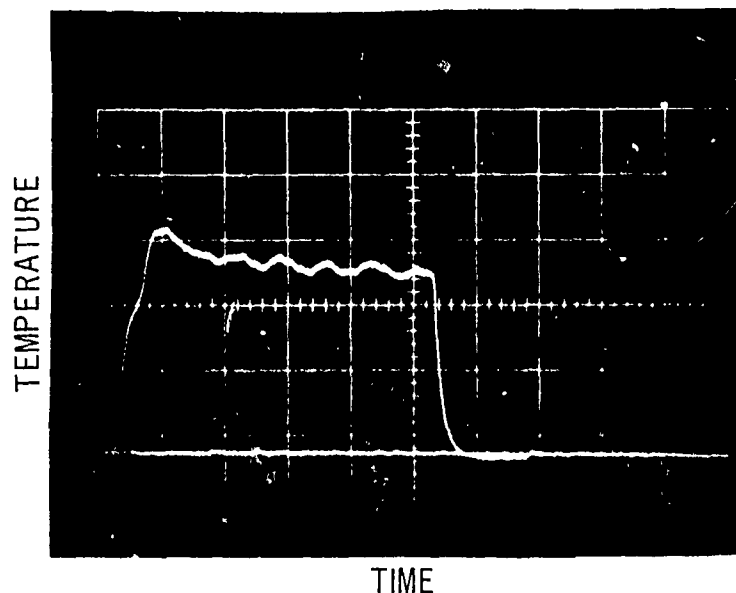


Figure 11 Typical Surface Temperature Trace for HTPB

Temperature data were obtained simultaneously with mass loss data. Surface temperature data were treated in the same manner as mass loss data, i. e., averaged from five individual points with standard deviation obtained by the range method. In the mass loss rate determination, the induction period was ignored, which is permissible because of the exponential dependence of rate upon surface temperature.

3. OTHER EXPERIMENTS

a. Thermal Properties

Measurements of heat capacity and thermal conductivity, which also yield thermal diffusivity given the density, were made in order to observe if there were significant differences between binders and to obtain quantities for use in an energy balance or in analyses involving the solid phase thermal wave. Heat capacity was measured by a standard water calorimeter technique. Thermal conductivity was measured using samples of binders prepared to have parallel plane surfaces as a slab conductor, adaptable to a CENCO Model 77555 conductivity apparatus. Reported densities were checked by weight-volume displacement measurements.

b. Gas Sample Analysis

Gas samples drawn from the test chamber were analyzed with a Perkin-Elmer Model 270 mass spectrometer equipped with a Bendix gas/liquid/solid inlet system. Tare outputs were obtained for the machine background and for nitrogen drawn from the test chamber in the absence of a sample. Output intensities for each sample were normalized with respect to peak intensities.

It was originally planned to use a gas chromatography method of analysis. However, this proved infeasible because of the varied products covering a broad range of molecular weights. Products proved to be more elaborate than calculated from equilibrium thermochemistry.

After the gas sample was drawn, the gases resided in the samples at room conditions for a considerable length of time (of the order of an hour) prior to analysis in the mass spectrometer. Consequently, the results are open to the question that the species analyzed are not representative of gases issuing from the decomposing surface. However, results from the more elaborate flash mass thermal analysis technique (40), whereby products are analyzed through a Bendix time-of-flight mass spectrometer as they are evolved, reveal a product distribution consistent with that reported herein (Section V).

SECTION V

EXPERIMENTAL RESULTS

1. PYROLYSIS DATA IN NITROGEN

a. Optimization and Effect of Exposure Time

Tests were conducted with the HC-434 CTPB binder in order to ascertain useful ranges of exposure times as a function of imposed heat flux. These tests would form a basis for initial exposure time selections for future tests with other binders, and establish the limitations of the technique with respect to achieving equilibrium data.

If the exposure time is too short, the mass loss and surface temperature data will involve an excessive proportion of startup transient conditions. This is unsatisfactory for the purpose of constructing an Arrhenius plot, or for relating mass loss to energy input in order to deduce heat of decomposition from an energy balance. If the exposure time is too long, the sample may regress out of the focal volume of the radiant source, or the sample surface condition may enter a new nonequilibrium process (e.g., char buildup), or smoke in the chamber may build up excessively, notwithstanding the purge. These, also, are unsatisfactory if the effect is to materially alter the mass loss rate, surface temperature, or imparted heat flux. Consequently, it was desired to seek an intermediate range over which equilibrium conditions are maintained.

Mass loss results at a heat flux of $100 \text{ cal/cm}^2\text{-sec}$ are shown in Figure 12. The threshold time was approximately 80 milliseconds. A reasonable straight-line region, indicative of equilibrium, appears between exposure times of $\frac{1}{4}$ and 2 seconds. At an exposure time of 3 seconds, something caused the mass loss rate to decrease and the error percentage to increase; departure from equilibrium also was indicated by the surface temperature output. The percentage error is also increased at an exposure time of $\frac{1}{8}$ second; startup effects are still significant over this interval, as confirmed by the surface temperature output.

Similar plots result in the envelope of exposure times versus heat flux presented in Figure 13. Heat fluxes of 15, 35, 85, 100, 135, 180, 200, and $220 \text{ cal/cm}^2\text{-sec}$ were examined. It is observed that the range shifts to shorter times and is narrowed as heat flux increases. The envelope appeared to be closed at $220 \text{ cal/cm}^2\text{-sec}$ as the data became unsatisfactory with respect to equilibrium and reproducibility, and the data at $200 \text{ cal/cm}^2\text{-sec}$ appeared marginal. At the other extreme, some tests were conducted at 3 and $7 \text{ cal/cm}^2\text{-sec}$ over exposure times ranging from 5 to 8 seconds; these conditions were dropped because surface temperatures were not appreciably different from those at $15 \text{ cal/cm}^2\text{-sec}$, and reproducibility was not as good.

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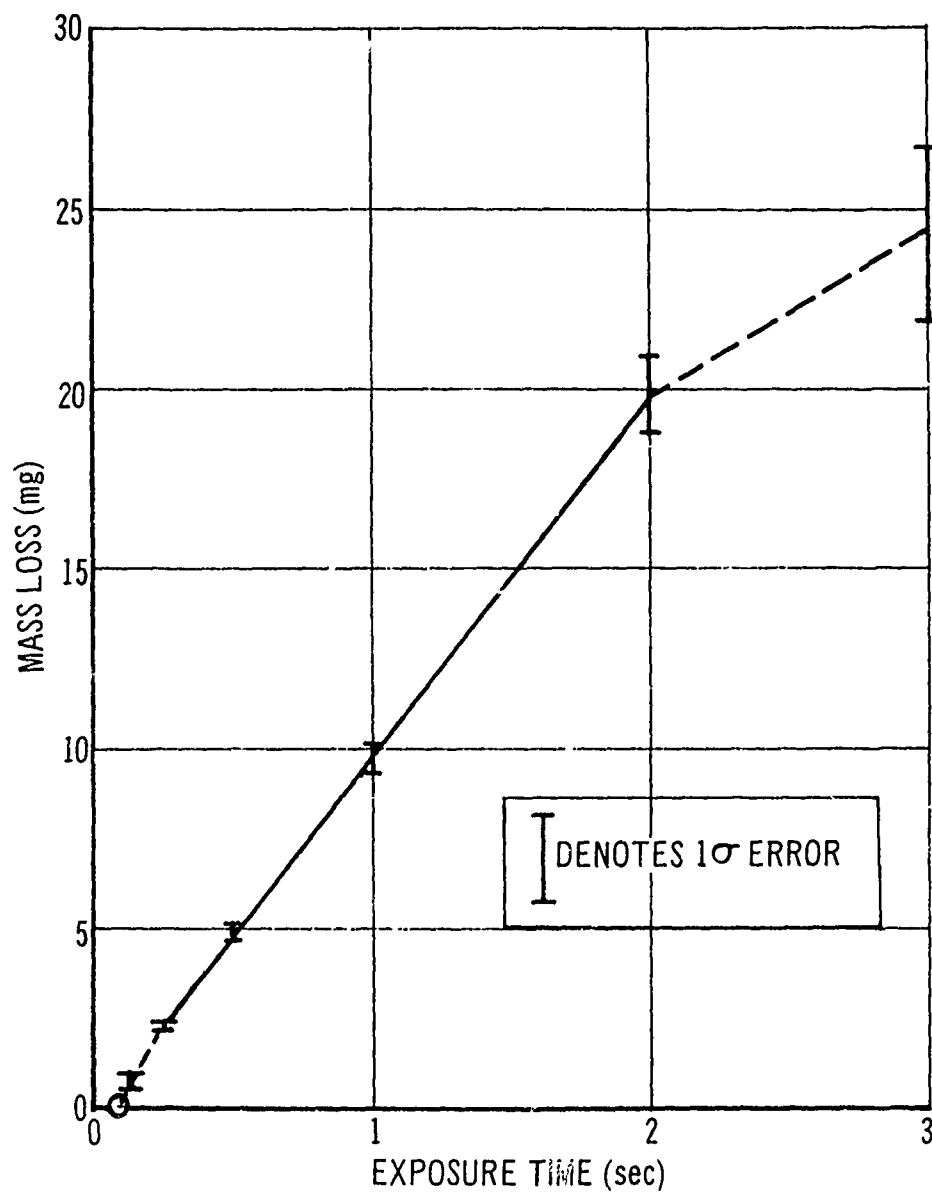


Figure 12 Mass Loss versus Exposure Time for CTPB at 100 cal/cm²-sec

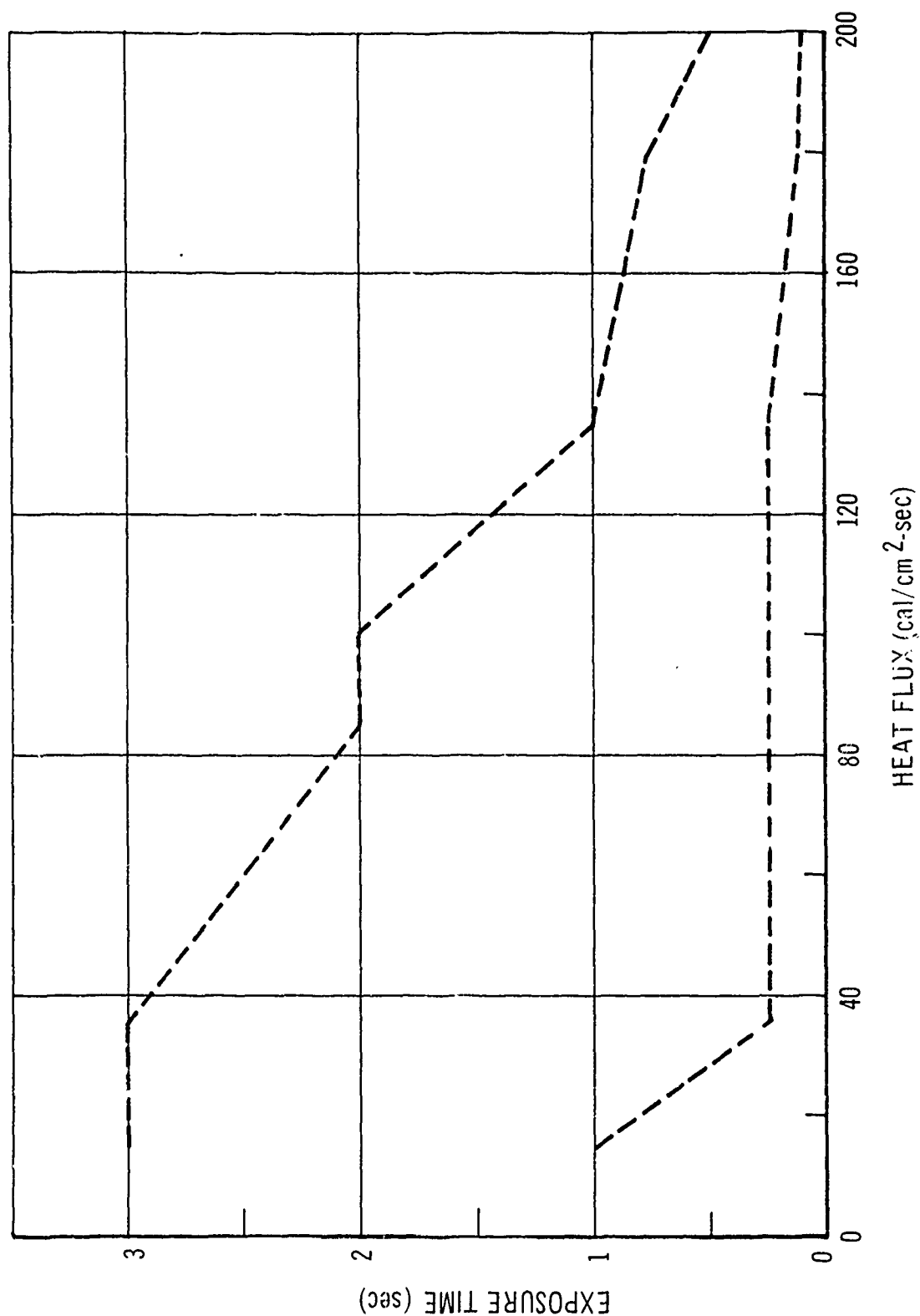


Figure 13 Range of Optimum Exposure Times Determined for CTPB

b. Effect of Heat Flux

The essential purposes for varying heat flux are to study binder decomposition under representative combustion conditions and to determine variations in mass loss rate and surface temperature sufficient to construct a reasonable Arrhenius plot.

An imparted heat flux of 200 cal/cm²-sec corresponds to the heat flux that would be calculated to sustain a propellant burning rate of approximately 0.4 in./sec. Such a burning rate is within the range of burning rates shown in Figure 1 for the common hydrocarbon formulations at 1000 psi. Assuming constant propellant surface temperature, and neglecting latent heat of decomposition (or assuming exothermic condensed phase processes neutralizing endothermic processes), the heat flux necessary to sustain burning rate is proportional to the burning rate sustained.

The range of surface temperatures acquired by varying heat flux from 7 to 200 cal/cm²-sec is shown for HC-434 CTPB in Figure 14. It is observed that the binder surface temperature increases with heat flux in an accelerating fashion, and that the error increases at the highest heat fluxes. The range of surface temperatures is adequate to construct an Arrhenius plot for the purpose of extracting kinetics constants; the plot will not be so compressed as to be clouded by the nonreproducibilities.

The Arrhenius plot for the HC-434 CTPB binder at 1 atmosphere is presented in Figure 15. Data for various exposure times within the acceptable range are included. The kinetics prefactor is determined to be 12.8 gm/cm²-sec, and the activation energy is 10.5 kcal/mole.

A combined plot showing the results for the various binder materials is presented in Figure 16. A wide range of behavior is evident. Over the range of heat fluxes from 15 to 200 cal/cm²-sec, it is observed that fluorocarbon exhibits the highest surface temperatures (1394 to 2550°C) and polyurethane the lowest (471 to 768°C). Polysulfide exhibits a relatively wide range of surface temperatures, most responsive to heat flux in this respect. The Arrhenius plots for HTPB and PBAN are virtually identical, and those for the two CTPB variations are nearly identical. It also is noteworthy that many of the binders exhibit approximately the same regression rate at 680°C, which is in the vicinity of reported surface temperatures for AP and AP-hydrocarbon propellants (10). The significance of the convergence of the lines is that changes in activation energy are being compensated by changes in prefactor; similar values of the ratio $E/\log A$ often indicate similar mechanisms.

Data are not included for the cured DEXSIL carborane because the data were unacceptable in samples not containing AP. The surface temperature would continually climb and substantially undulate. Post-test examination of surfaces revealed a white, crusty char that was apparently forming, heating, and sloughing off.

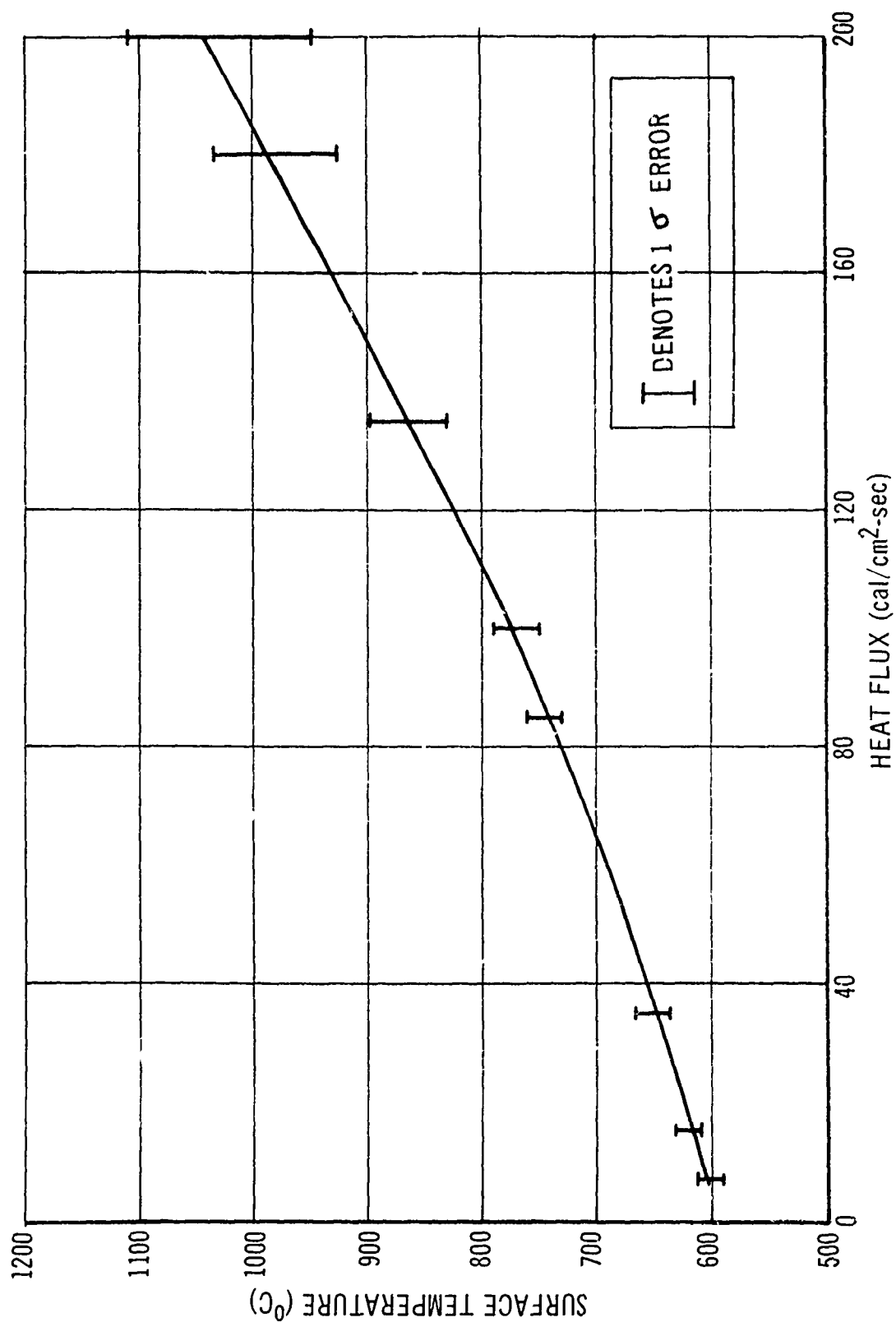
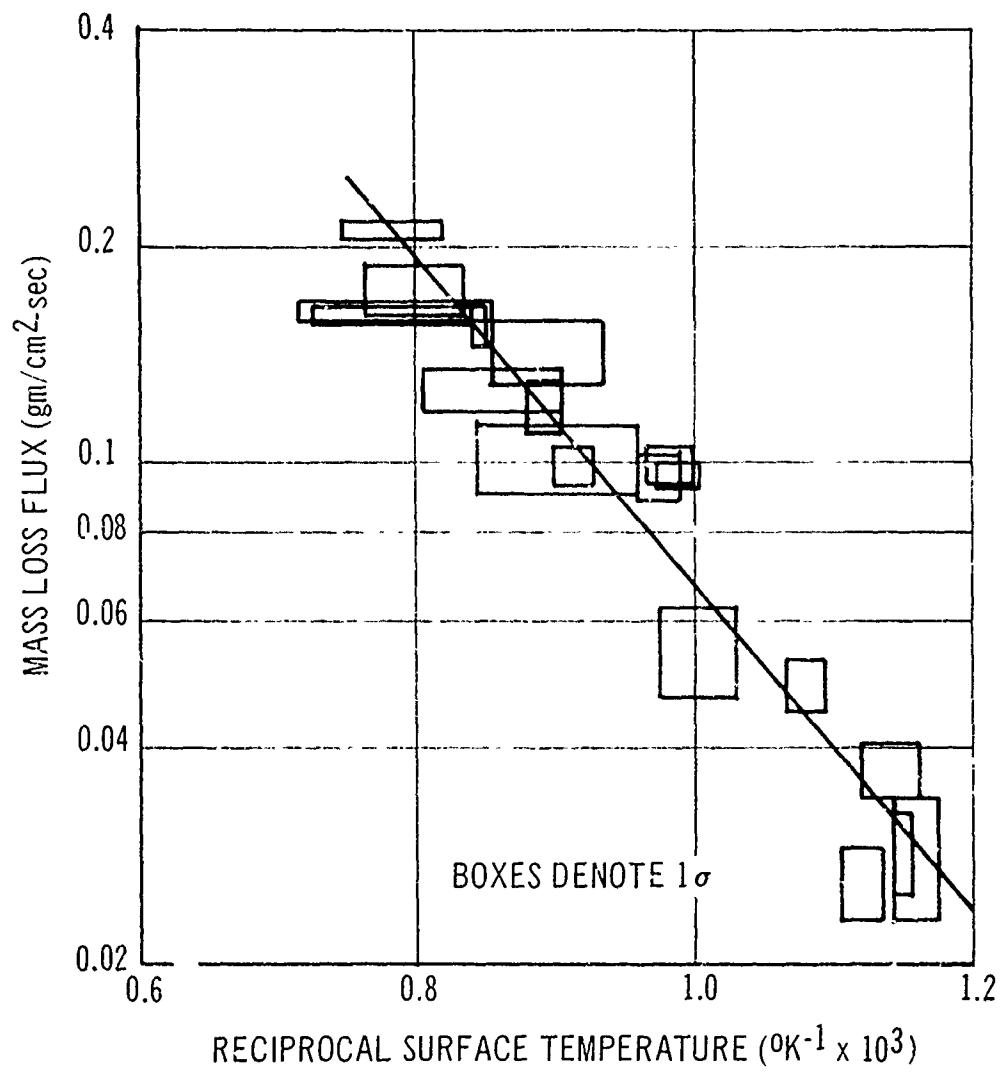
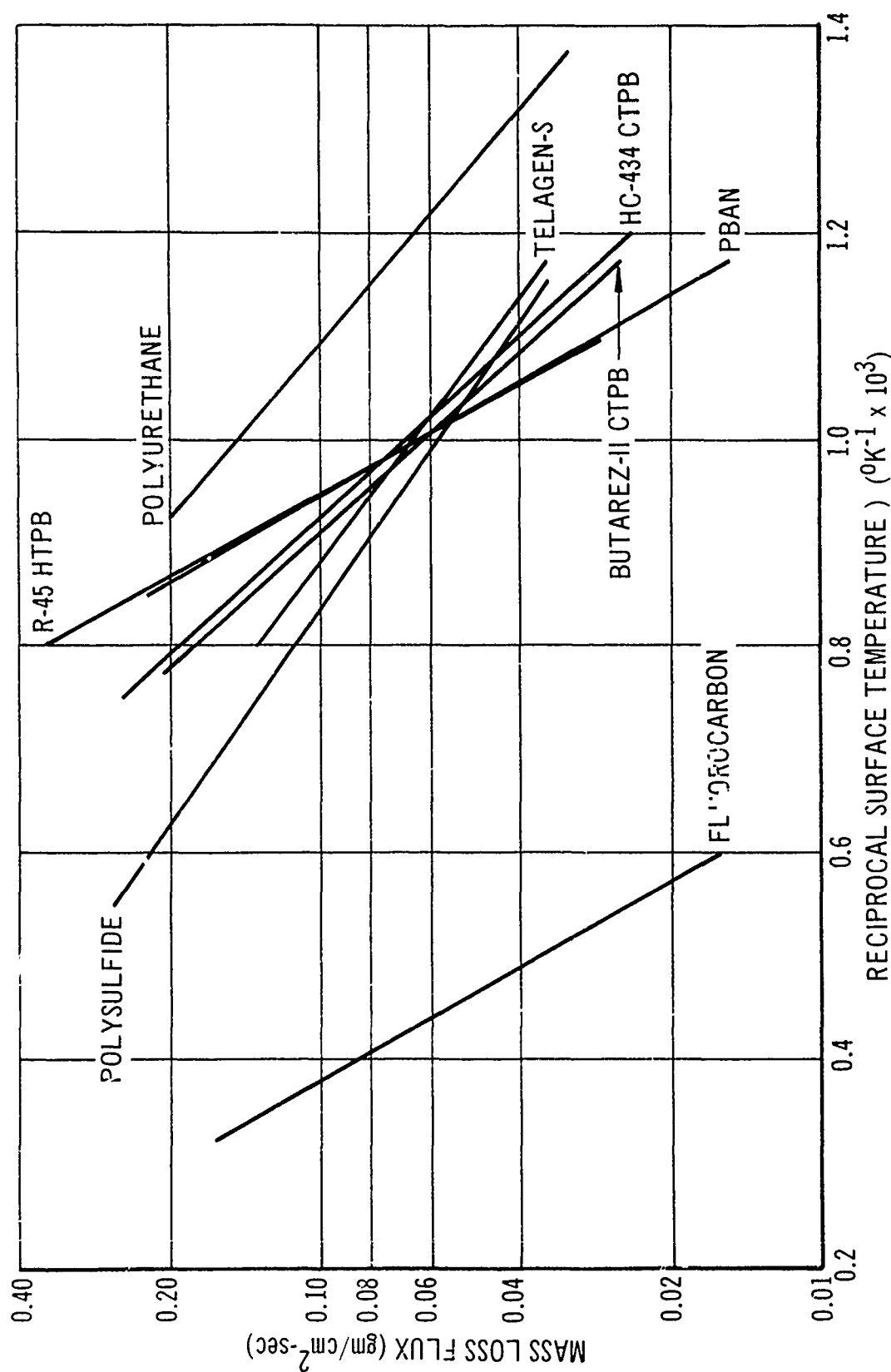


Figure 14 Variation of Surface Temperature with Heat Flux for CTPB Binder

Figure 15 Arrhenius Plot for HC-434 CTPB in 1 Atmosphere of N₂

Figure 16 Arrhenius Plots for the Various Binders in 1 Atmosphere of N₂

A summary of the kinetics constants is presented in Table III. The CTPB and polyurethane binders exhibit similar activation energies, but differ significantly in the prefactors; Telagen and polysulfide form a second such group; HTPB, PBAN, and fluorocarbon form a third such group, the HTPB and PBAN being equivalent to each other. Across these groups, the activation energies are within a factor of two, and the values are in such a low regime as to be indicative of a weak-link degradation process or a physical process such as boiling. Regarding values of $E/\log A$, one group is formed by CTPB, Telagen, and polysulfide; a second group is formed by HTPB, PBAN, and polyurethane, differing from the first group within a factor of two. Fluorocarbon, having thermal resistance applications (apart from its use as a binder), has a significantly different value of $E/\log A$; this appears to be the only important difference between the binders.

c. Effect of Pressure

For samples not containing AP, the effect of pressure was explored by testing over the range 15 to 100 cal/cm²-sec at 100 psia and, because of apparatus limitations, at 50 cal/cm²-sec at 1000 psi. These conditions were tested for HTPB, CTPB, PBAN, and polyurethane. Limited testing was conducted for Telagen, polysulfide, and fluorocarbon at 250 psia. No significant or consistent effect of pressure was found, either by surface temperature at a given heat flux or by the position of the result on the Arrhenius plot. The Arrhenius plot is exemplified for CTPB in Figure 17, superimposing the pressure data upon the 1 atmosphere line and envelope formed by box extremities.

Although it was not possible to measure surface temperature at combined conditions of 200 cal/cm²-sec and 1000 psi, tests were nevertheless conducted with CTPB and HTPB at least in order to compare mass loss. The mass loss at 1000 psi was increased by 3 percent and decreased by 9 percent, respectively, compared to results at 1 atmosphere, which are within the error bands.

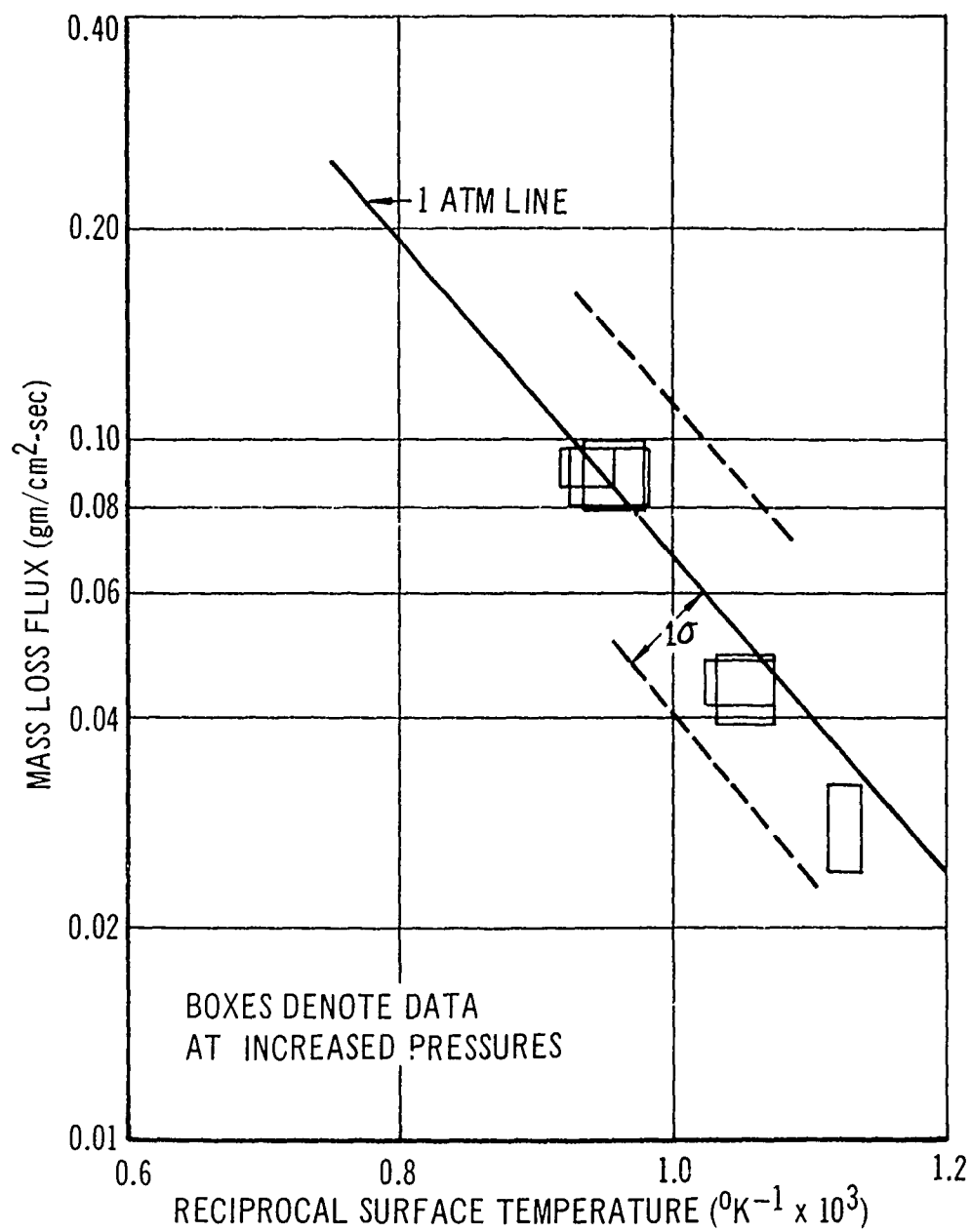
d. Effect of the Presence of Ammonium Perchlorate

In general, surface temperatures were increased somewhat with the presence of the 10-percent AP (40 μ) for a given imposed heat flux. The effect is illustrated for PBAN in Figure 18. This effect was observed for all binders except fluorocarbon. Although no effect of AP was seen for fluorocarbon, the high surface temperatures associated with fluorocarbon may have masked it. Increasing pressure in samples containing AP produced no additional effect, as was the case in samples not containing AP. Testing was conducted up to 1000 psi for AP-containing CTPB, PBAN, polyurethane, and polysulfide; HTPB without catalysts, Telagen, and fluorocarbon were limited to 250 psi.

Although surface temperature increased at a given heat flux, the mass loss also increased such that there were no significant displacements from the Arrhenius plot for the binder without AP. The absence of an effect of AP on the Arrhenius plot is illustrated for PBAN in Figure 19, superimposing all AP data upon the no-AP line and envelope formed by box extremities.

TABLE III
KINETICS CONSTANTS FOR THE VARIOUS BINDERS

	<u>Prefactor, A,</u> <u>(gm/cm²-sec)</u>	<u>Activation Energy, E,</u> <u>(kcal/mole)</u>	<u>E/log A</u>
CTPB (HC-434)	12.8	10.5	9.49
CTPB (Butarez II)	11.6	10.5	9.86
Polyurethane	49.4	10.2	6.02
Telagen-S	7.3	9.0	10.4
Polysulfide	5.6	8.7	11.6
HTPB	299	16.9	6.83
PBAN	270	16.7	6.87
Fluorocarbon	2.6	17.0	40.9

Figure 17 Effect of Pressure on CTPB Pyrolysis in N₂

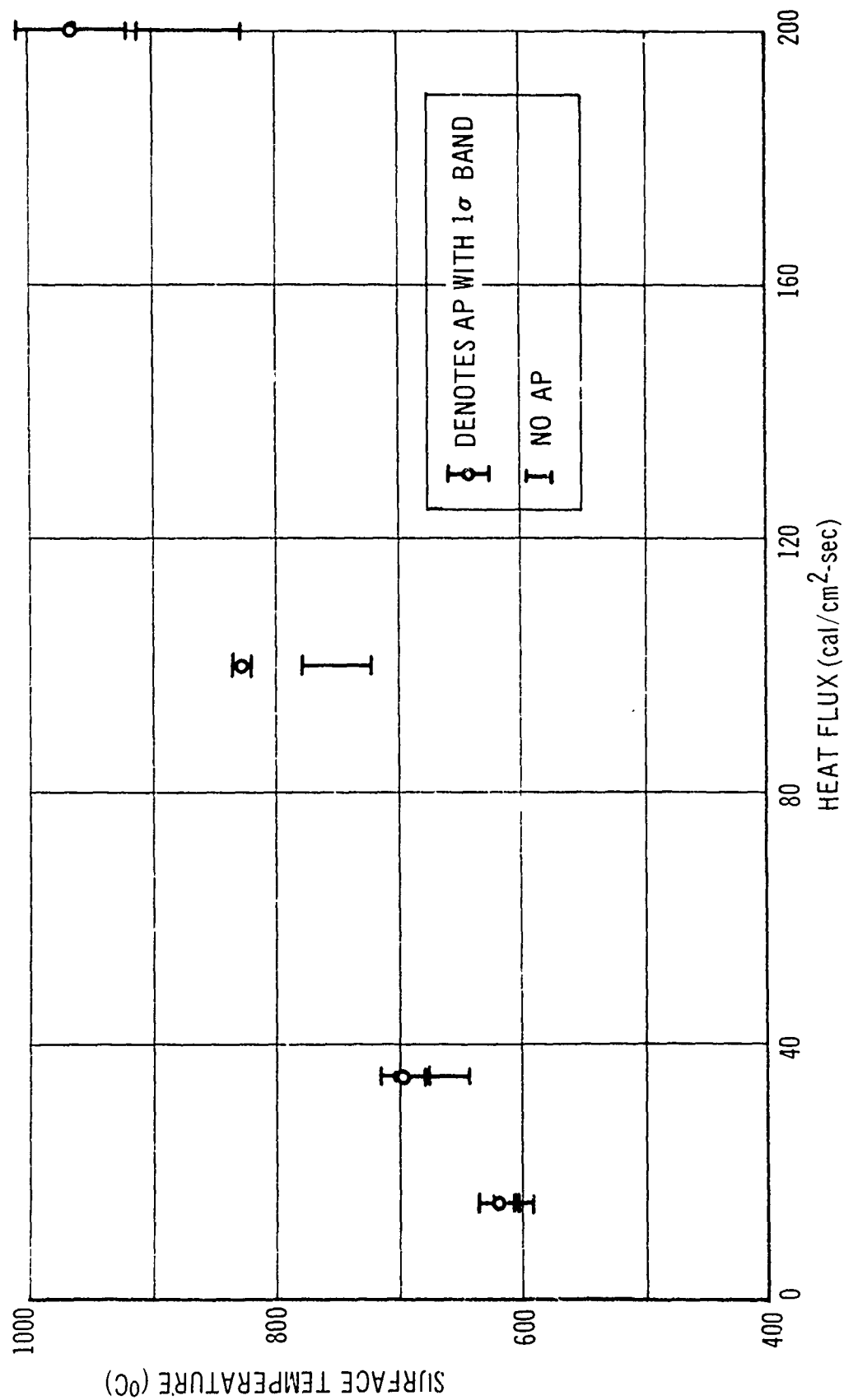


Figure 18 Effect of Ammonium Perchlorate on Surface Temperature for PBAN Binder

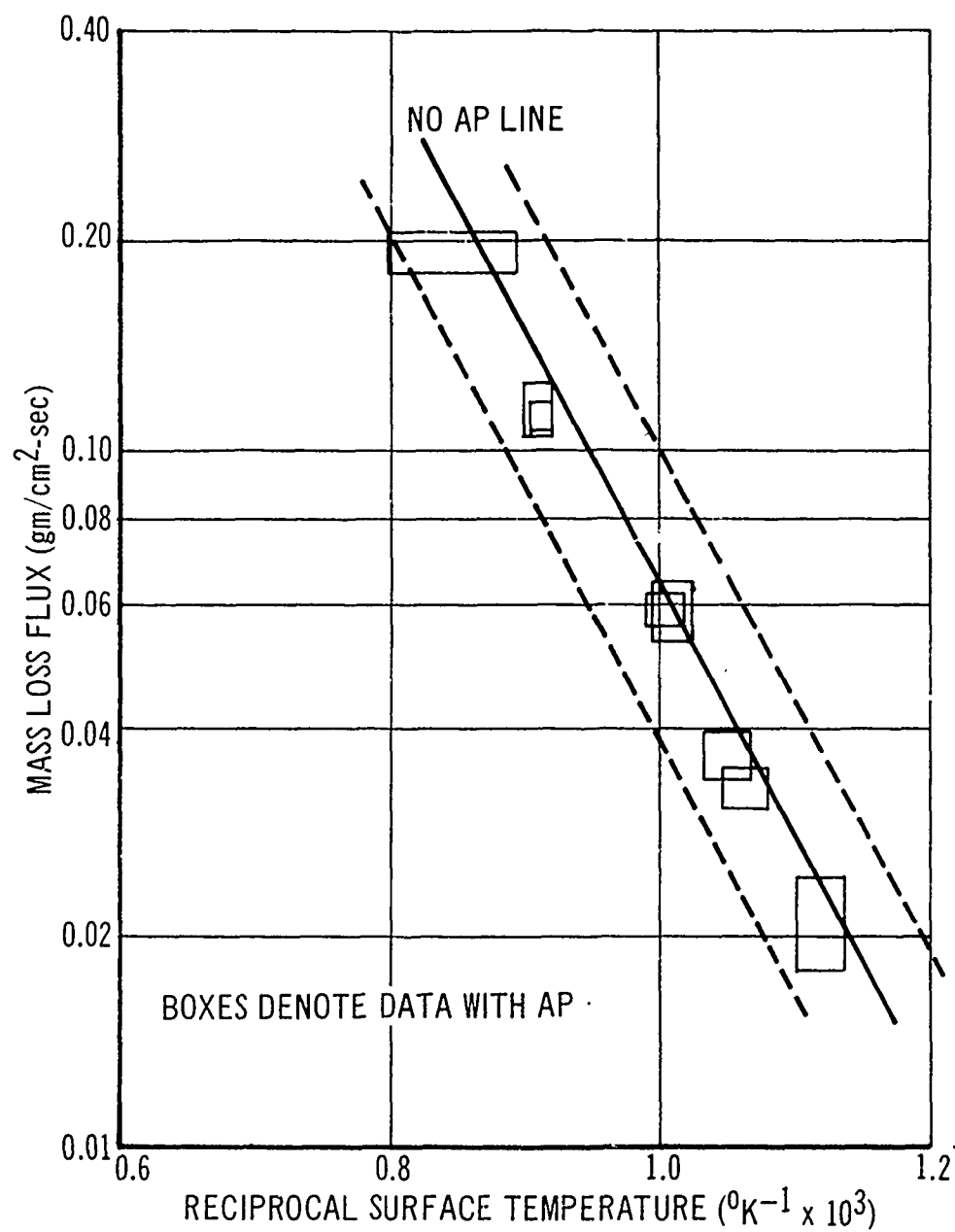


Figure 19 Effect of Ammonium Perchlorate on PBAN Pyrolysis in N₂, 1 Atmosphere to 1000 psi

A significant effect of AP was observed in the carborane binder in that acceptable equilibrium data were achievable. Post-test examination of the sample surface indicated that the white, crusty char had become a loose powder in lesser amount. The Arrhenius plot for carborane with AP is presented in Figure 20. The activation energy is a low 4.4 kcal/mole, and the prefactor is a correspondingly low 0.2 gm/cm²-sec. The surface temperatures ranged from 820 to 2164°C, which is nearly as broad a range as that exhibited by polysulfide but is shifted toward the high temperatures exhibited by fluorocarbon. A similarity to the fluorocarbon is the relatively low mass loss flux for a high surface temperature (compare Figure 20 with Figure 16). Another similarity to the fluorocarbon is the relatively high value of $E/\log A$; if all prefactors were arbitrarily increased by a factor of 10 so that the carborane would not give a negative value, the $E/\log A$ for carborane and fluorocarbon would be approximately the same and substantially higher than for the other binders. This carborane, like fluorocarbon, has applications in the area of thermal resistance.

For the carborane containing AP, there was no significant effect of raising the pressure to 250 psia either on the surface temperature or on the Arrhenius plot. However, at 1000 psi, the surface temperature markedly increased (from 1162 to 1835°C at 50 cal/cm²-sec); the movies (discussed in subsection 3) indicated a presence of flames on the surface on the microscopic scale, revealing an ignition rather than a pyrolysis condition. Ignitions were not observed in binders not containing catalysts.

Other effects of AP are discussed in the following subsection.

e. Effect of Catalysts

Catalysts nBf and DEXSIL carborane were incorporated into the HTPB at concentrations equivalent to the 2-percent level in a propellant of 86-percent solids. For each catalyst, the binder was made with and without the 10-percent AP.

In the case of nBf, with or without AP, there were no significant effects compared to the results of HTPB without nBf. Surface temperatures and positions on the Arrhenius plot were as though the nBf were absent. The effect of AP in increasing surface temperature was the same with nBf as without it. Increasing pressure to 1000 psi had no effect except for an ignition, which occurred at 200 cal/cm²-sec and 250 psia with AP; ignition did not occur at 50 cal/cm²-sec and 1000 psi. All nBf data are superimposed upon the no-nBf Arrhenius line and envelope in Figure 21.

In the case of carborane included as a plasticizer-catalyst results were the same as for nBf. An ignition also was detected for the condition 200 cal/cm²-sec and 250 psia with AP.

f. Effect of Aluminum

Testing with HTPB containing aluminum was limited to motion picture observation. Surface temperature measurements were precluded by the large aluminum agglomerates formed. It appeared that one giant

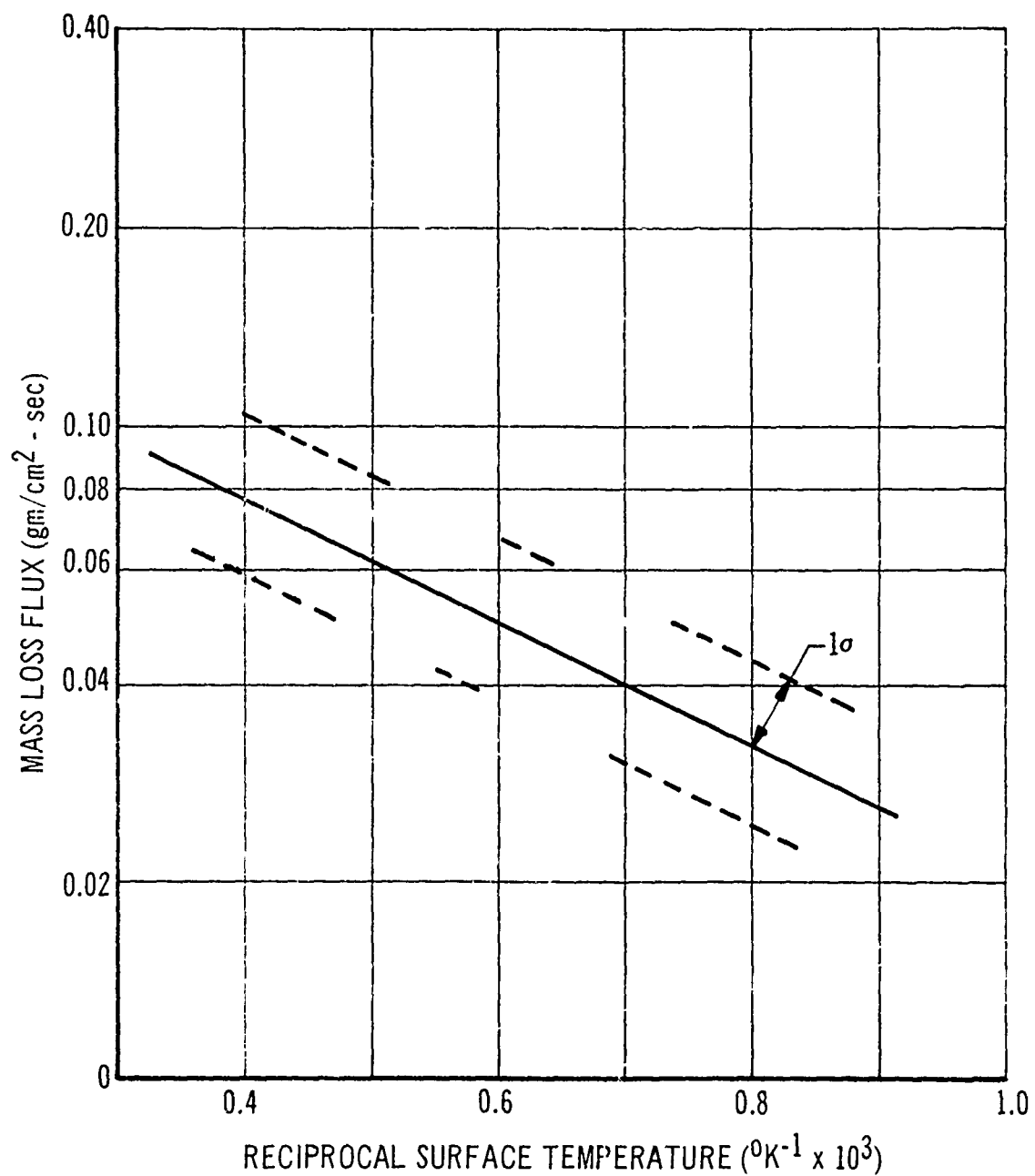


Figure 20 Arrhenius Plot for Polymerized Dexsil Carborane Containing Ammonium Perchlorate in N₂

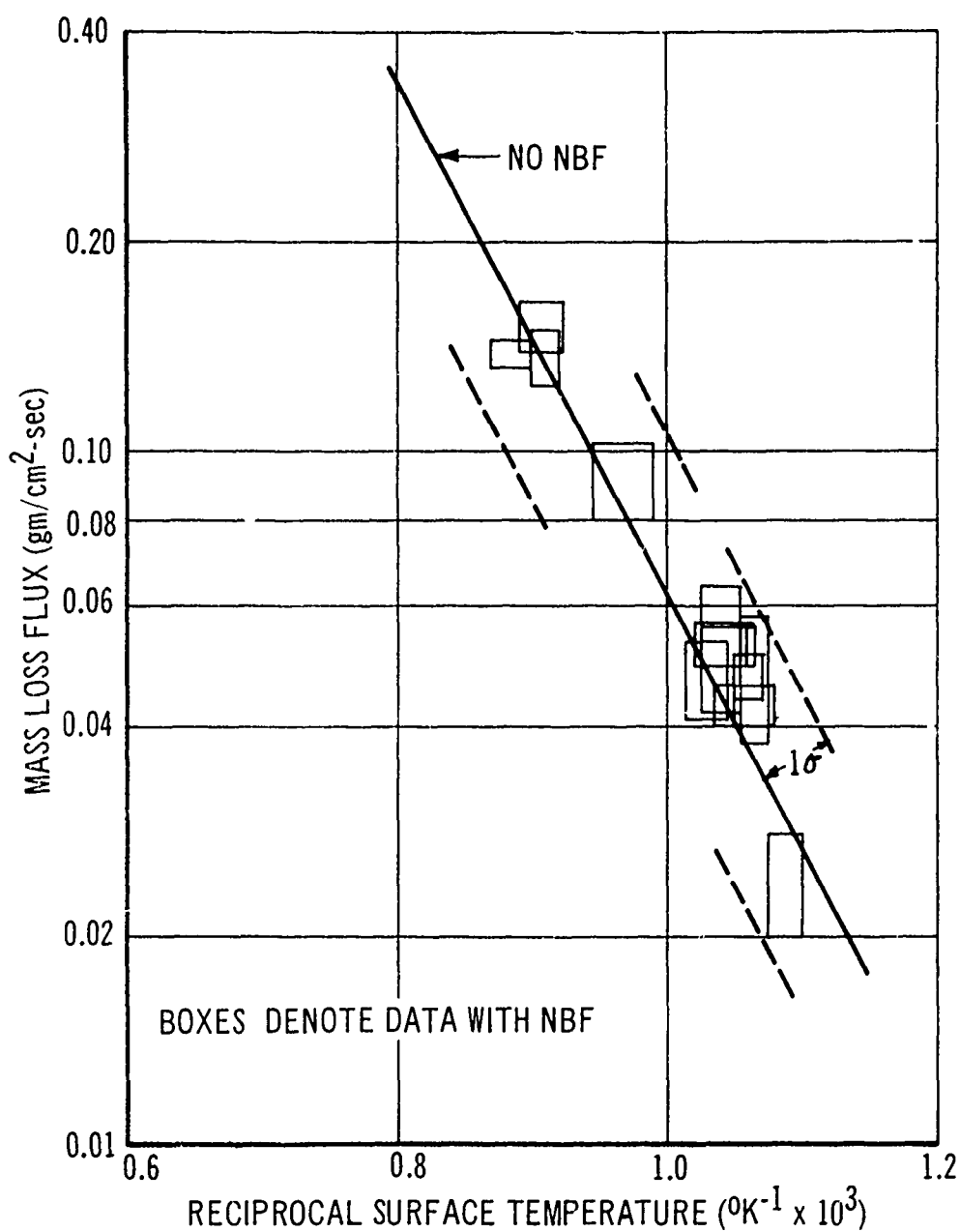


Figure 21 Effect of nBf on HTPB Pyrolysis in N₂, With and Without Ammonium Perchlorate, 1 Atmosphere to 1000 psi

agglomerate was progressively forming from smaller agglomerates as time increased. In the initial portion of the test, very small particles could be seen flowing away from the surface. Then agglomerates formed, became set, and attached to adjacent agglomerates; no more particles could be seen leaving the surface. The attachment process progressed and the mass commenced to glow with increasing intensity.

2. PYROLYSIS DATA IN OXIDIZING GASES

a. Selection of Oxidizing Gases

Considerable attention was given to the question of the proper oxidizing environment to represent possible processes occurring in AP-oxidized composite propellants. The logic, in essence, followed the probable course of AP decomposition as it might reasonably manifest itself in a propellant.

Perchloric acid, available commercially in a relatively safe hydrated form, was considered first. However, to be useful for the purposes of the pyrolysis experiments for this program, it would have to be delivered to the test chamber as a gas and maintained as a gas, which necessitates maintaining temperatures above its boiling point of 200°C. Such would introduce uncertainties as to local condensation on surfaces, effects of preheating the binder sample, and materials compatibility considerations not otherwise necessary. Another question raised was that perchloric acid is only an initial decomposition product of AP and perhaps not the chemical directly responsible for interaction with binder in a propellant.

Consideration was then given to chlorine dioxide, a decomposition product of perchloric acid known to be highly reactive. It is a gas at room temperature, but involves handling, storage, and safety problems and was not found to be readily available commercially. Furthermore, it would have to be diluted considerably to avoid hypergolic reaction with the sample at room temperature, which would cloud the pyrolysis data.

Some researchers believe that the efficacy of perchloric acid, through its chlorine oxide decomposition products, results from the ease of heterogeneous dissociation of chlorine oxides into chlorine atoms (41). Hypergolicity with fuel surfaces at room temperature is believed to follow from this dissociation, whereby the chlorine atoms attack the fuel. Chlorine also can dissociate into chlorine atoms, but not nearly as easily. Therefore, chlorine gas is not hypergolic with polymers at room temperature, but heterogeneous attack of the polymer might be expected if the polymer surface is heated to a degree that the chlorine would dissociate at the surface. The range of surface temperatures measured in nitrogen was such that a degree of dissociation sufficient to cause some observable effect would be expected; in effect, chlorine undiluted would take the place of chlorine dioxide considerably diluted. The only problem would be to avoid gas phase reactions, which would be expected to restrict test pressures. Testing with chlorine has a number of practical advantages, which also rendered chlorine attractive for selection.

Oxygen also was suggested from the standpoint of representativeness and practicality (42). Although it is well established that oxygen is not nearly as reactive as perchloric acid or its decomposition products for the process of oxidative polymer degradation (10), it can produce this process, particularly in the presence of catalysts (42). Consequently, observations at the heating rates and surface temperatures achievable in this program would be warranted. Again, however, care would have to be exercised to avoid flames in the gas phase. Air was selected to effect a dilution.

b. Effect of Chlorine

The effect of chlorine, with and without AP, was tested for CTPB, HTPB, polyurethane, fluorocarbon, and HTPB containing nBf. It was tested for carborane only in samples containing AP. It was found necessary to test at a pressure of 7 psia chlorine to avoid gas phase reactions; flames were revealed by the movies and the temperature data at 1 atmosphere of chlorine.

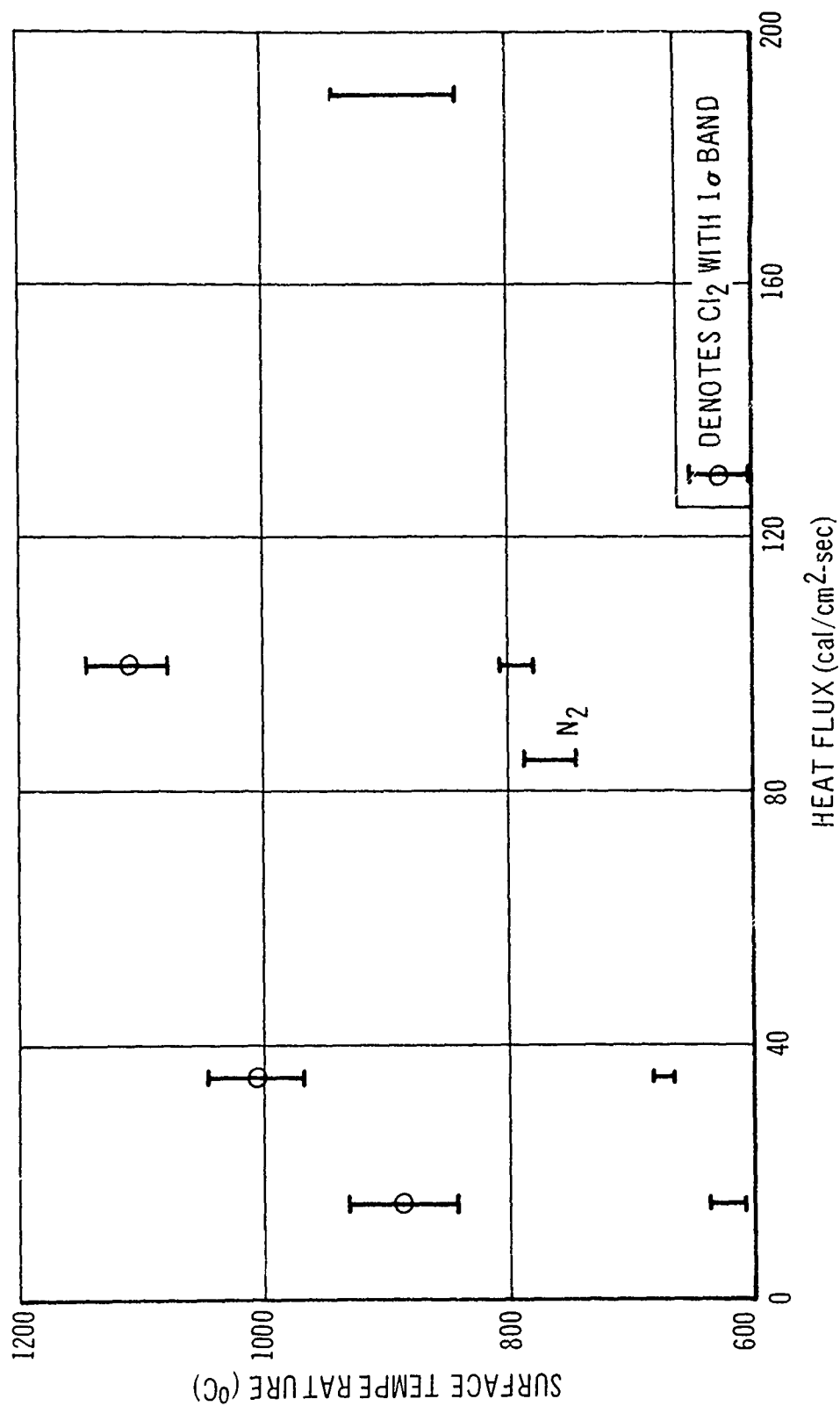
Four different effects were observed. One type of effect was common to CTPB, HTPB, and polyurethane. A second type was exhibited by the polymerized carborane. A third type was exhibited by HTPB containing nBf. Fluorocarbon exhibited unique aspects of each of the above three effects.

The first group, CTPB, HTPB, and polyurethane, was characterized by an increase in surface temperature for a given heat flux and by a downward shift in the Arrhenius line. The presence of AP, in chlorine, did not have the consistent effect of further raising the surface temperature that it had in nitrogen, and it did not further affect the location of the Arrhenius line (i. e., no effect of AP in chlorine for this group). The effects of chlorine were comparable in magnitude for CTPB and HTPB, but were to a lesser degree for polyurethane.

The effect on surface temperature for this first group is exemplified by HTPB in Figure 22. The increase is by several hundred degrees centigrade. In polyurethane, the increase was approximately 100°C. The effect on the Arrhenius plots for this group is summarized by Figure 23. It is noted that the slope of the CTPB line is increased so as to be similar to that for HTPB, but is not appreciably changed for HTPB or polyurethane.

In the case of the carborane containing AP, there was an increase in surface temperature in chlorine to the degree exhibited by polyurethane, and therefore a proportionately smaller effect. There was no effect on the position of the Arrhenius line, perhaps because it already was in a high-temperature, low-mass-flux regime.

A completely different kind of effect appeared for HTPB containing nBf, which was not further influenced by the presence of AP. The surface temperature again increased in chlorine over nitrogen, but it decreased with increasing heat flux. Results are shown in Figure 24.

Figure 22 Effect of Cl₂ on Surface Temperatures for HTPB Binder

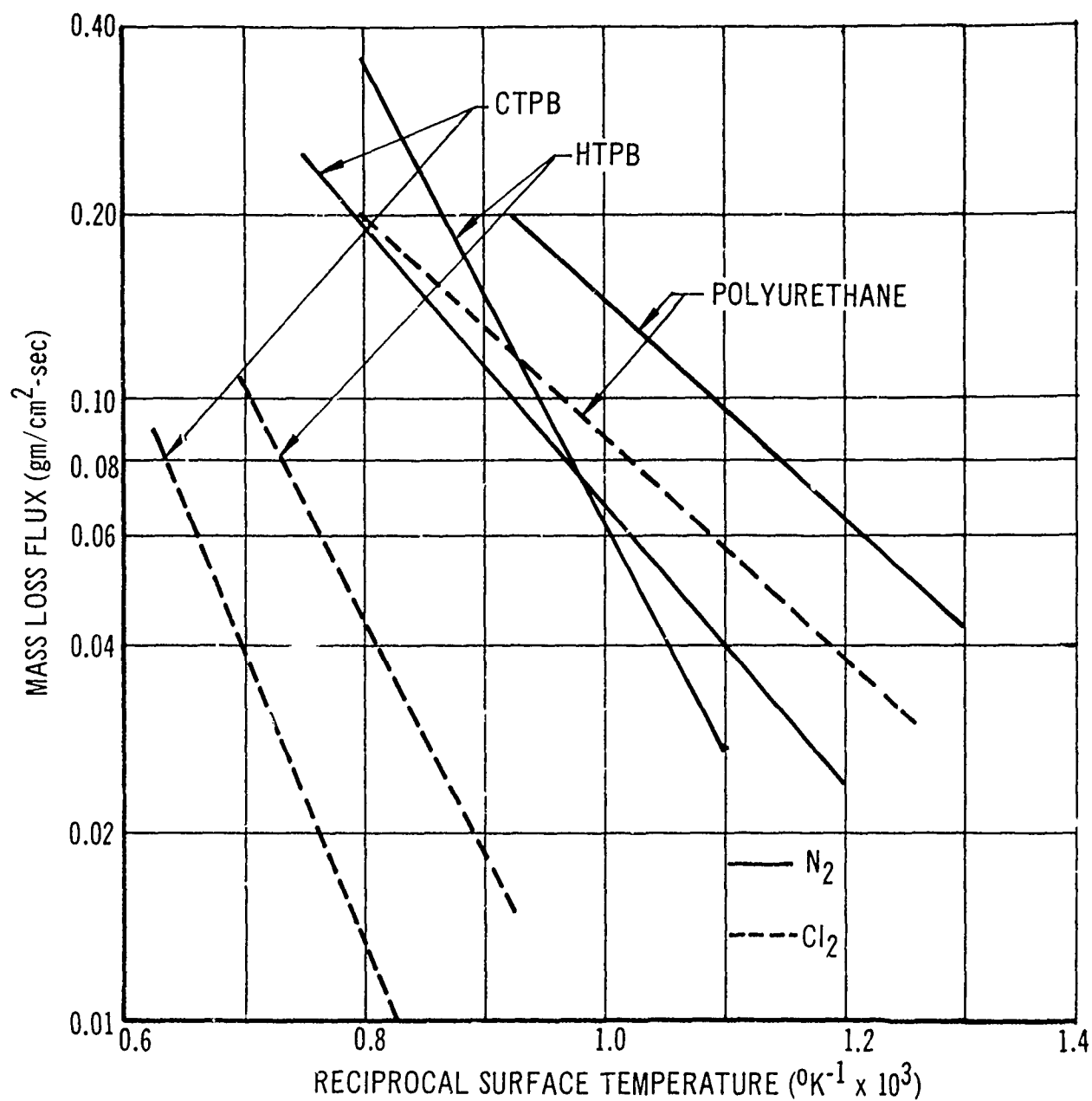
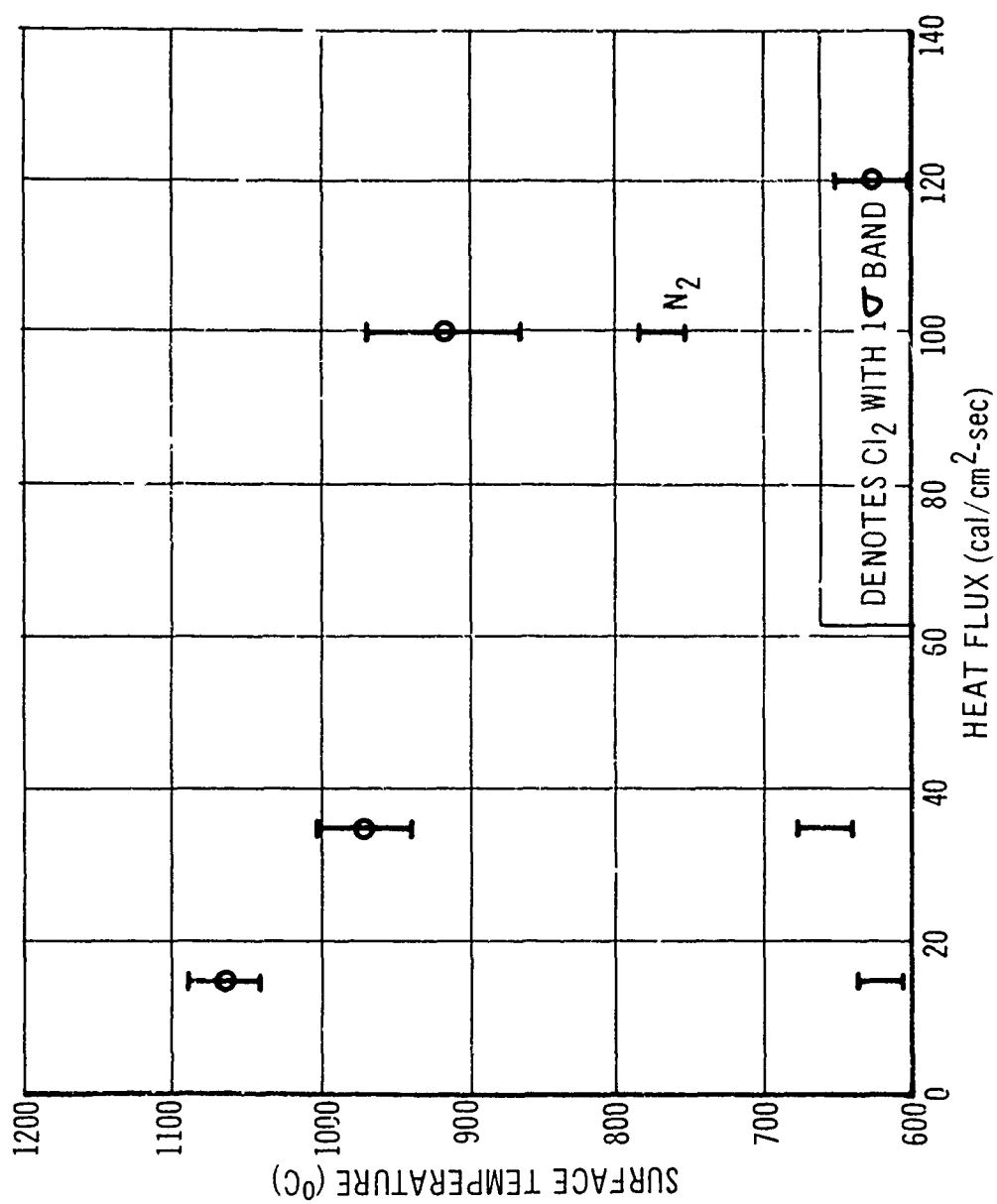


Figure 23 Effect of Cl₂ on Pyrolysis of CTPB, HTPB, and Polyurethane

Figure 24 Effect of Cl₂ on Surface Temperatures of HTPB Containing nBf

Because mass loss increased with increasing heat flux, the upshot is an increase in mass loss with decreasing surface temperature. Superimposition of the data upon the results in nitrogen, Figure 25, appears to indicate that the mechanism is a function of heat flux. There was no significant effect of AP.

A similar effect was observed for fluorocarbon containing AP. Surface temperature decreased with increasing heat flux while the mass loss increased with increasing heat flux. However, there were two variations: the surface temperature in chlorine was considerably less than in nitrogen, and the data are positioned above instead of below the Arrhenius line for nitrogen (Figure 26). Without AP, there was little change in surface temperature from nitrogen, and the data line up to form a new Arrhenius line displaced above the line for nitrogen. Therefore, without AP, the mechanism does not appear to be a function of heat flux (similar to type 1 and 2 effects); with AP, the mechanism does appear to be a function of heat flux (similar to type 3 effect). Unique to fluorocarbon is the result that chlorine enhances rather than depresses the regression rate.

c. Effect of Air

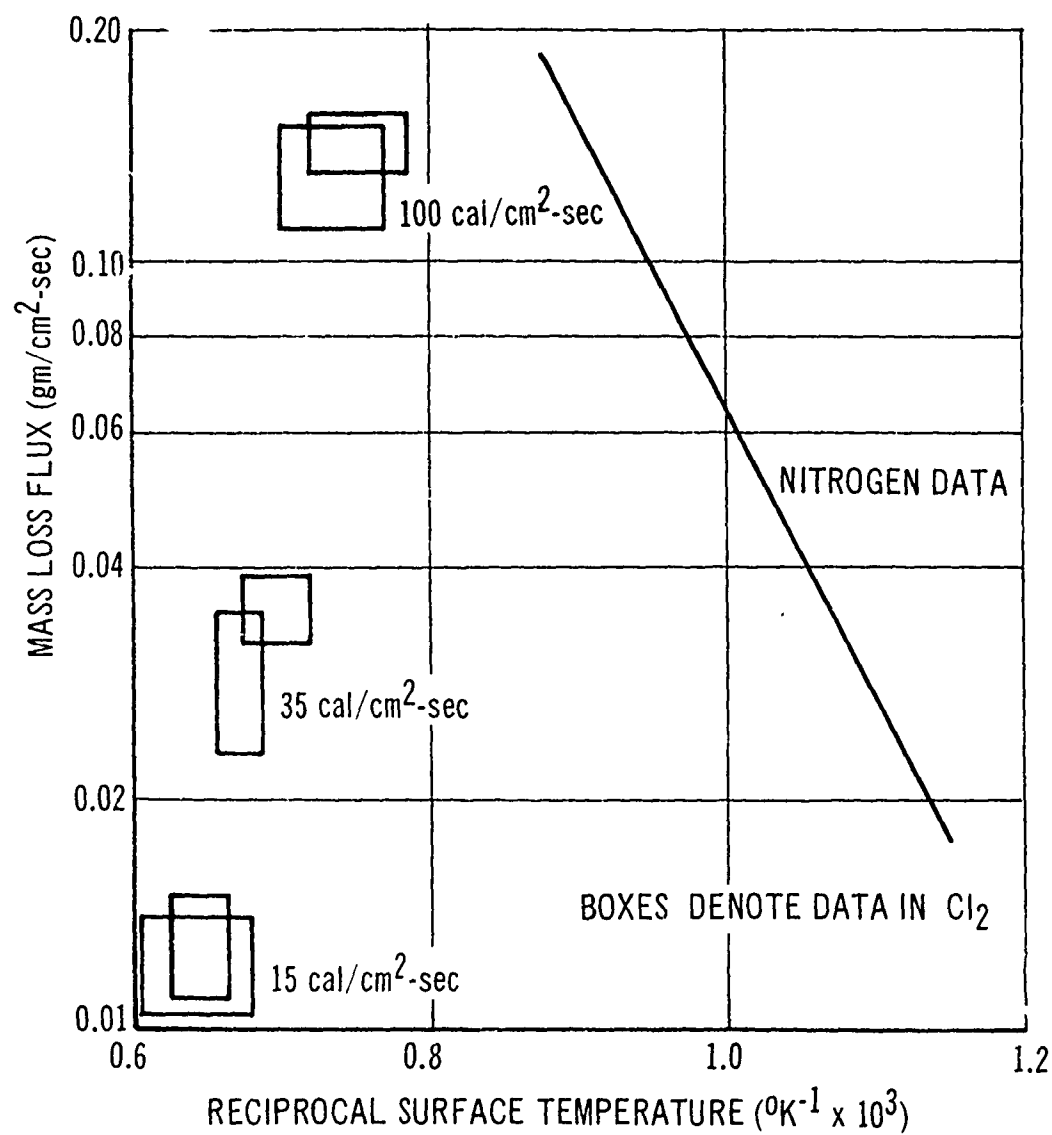
The effect of air was determined only for CTPB. Data were acquired at 7 psia, over the range 15 to 100 cal/cm²-sec, with and without AP. There was no effect of air on surface temperature at a given heat flux. However, the mass loss results changed significantly so as to increase the apparent activation energy. Results are summarized in Figure 27. There was no effect of AP.

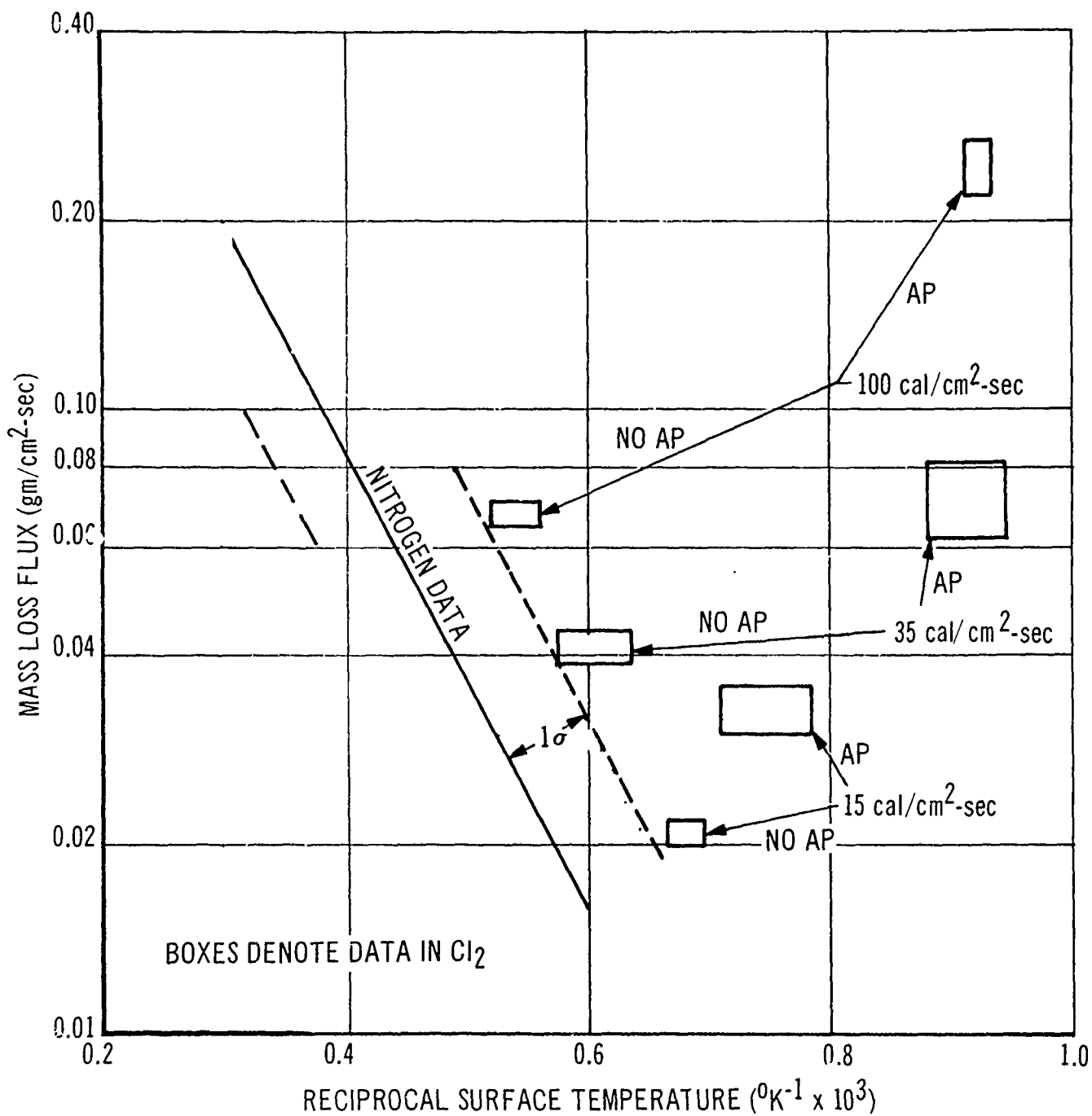
d. Comment

The effect of environmental gases, particularly Cl₂, were the largest in magnitude and some of the most interesting observed in the entire program. However, the possibility that the data were influenced by gas phase processes, such that true pyrolysis kinetics were not being measured, cannot be completely ruled out. The basis for selecting the pressure of 7 psia was a relative basis, to avoid gas phase processes, by comparing results at 1 atmosphere, 7 psia, and 3 psia.

At 1 atmosphere of Cl₂, streams of orange flames could be seen in movies, and the temperature output showed a staged rise characteristic of an ignition and an oscillatory behavior characteristic of flame interference. A considerable amount of carbonaceous material was evolved. At the lower pressures, the temperature output showed a single rise to an equilibrium value that was considerably lower in magnitude; however, the movies showed the gas to change from a transparent yellow-green to a transparent orange.

It is possible that changing heterogeneous reaction processes, i.e., oxidative degradation by chlorine, were being observed and measured. However, at this time, it is considered that the data should be treated with caution as possibly influenced by flame processes.

Figure 25 Effect of Cl_2 on Pyrolysis of HTPB Containing nBf

Figure 26 Effect of Cl₂ on Pyrolysis of Fluorocarbon

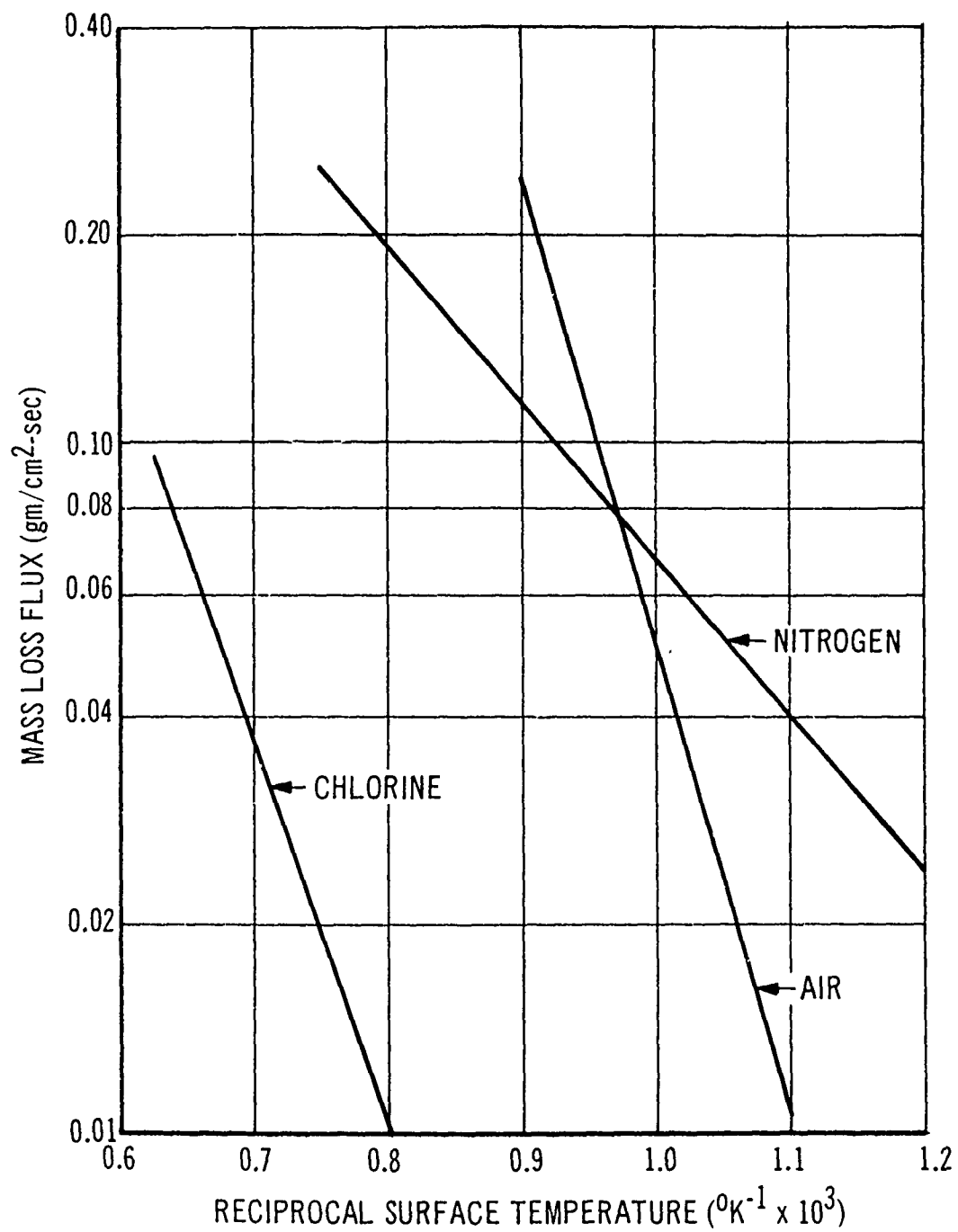


Figure 27 Effect of Environmental Gases on Pyrolysis of CTPB

3. MOTION PICTURE AND SURFACE OBSERVATIONS

a. Effects in CTPB and HTPB

Without AP, and in nitrogen, the CTPB exhibited a molten, boiling surface over the full range of heat flux and pressure. With increasing heat flux, the amount of black smoke issuing from the surface increased. As pressure increased, the boiling bubbles became smaller. At 1000 psi, the smoke issuing from the surface was white and, intermittently, a heavy globule of orange-brown smoke would come forth. A post-test photograph of the surface is shown in Figure 28a. This clear, smooth surface is characteristic of all CTPB tests in nitrogen.

The effect of including AP was the formation of some surface char. The char appeared as islands surrounded by rivers of boiling binder. A representative post-test photograph is shown in Figure 28b. Other observations were the same as those made during tests without AP, except that at 1000 psi there were puffs of white smoke superimposed on the stream of white smoke issuing from the surface.

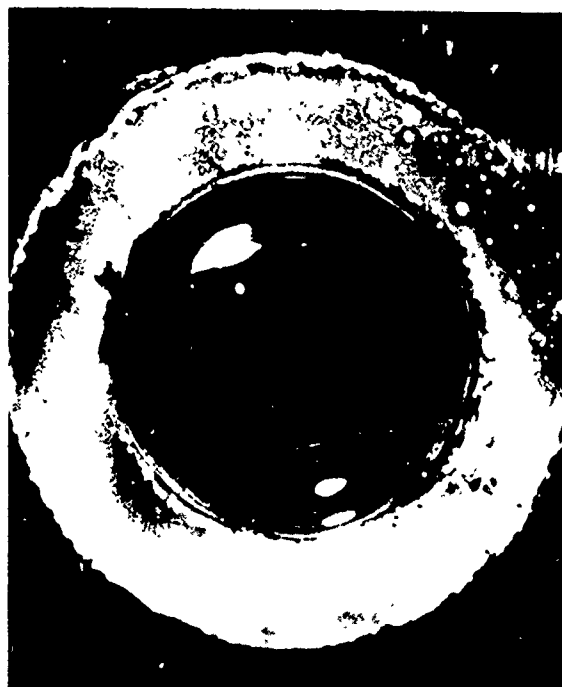
Chlorine produced a very dry surface, as shown in Figure 28c. At 1 atmosphere, streams of flame were evident in the movies and chunks of carbon were seen flying in all directions; the movies were blacked out within a relatively short time. At 7 psia, a boiling surface could be observed, but the surface had the same dry look upon post-test examination. The inclusion of AP in chlorine appears to result in the formation of local lumps of char superimposed on the smooth char (Figure 28d).

Observations of HTPB showed basically the same trends of behavior as CTPB except that the char formation was more pronounced. Figure 29a, corresponding to the conditions of Figure 28a, shows residual islands of char around which the molten, boiling surface could be seen in movies. The char was much more pronounced with AP. Figure 29b and c show the effect of heat flux with AP present, Figure 29c being the companion to Figure 28b. The dry, granular, fine structure becomes finer with increasing heat flux, and the boiling binder becomes rivulets. With chlorine and AP, the drier appearance of HTPB relative to CTPB is maintained; Figure 29d is the companion to Figure 28d.

In summary, the principal effect of AP or chlorine is to produce char. The principal effects of increasing heat flux are the production of black smoke and a more homogeneous char fine structure. The principal effects of increasing pressure are a reduction in the size of boiling bubbles and, at high pressure, a change in the color of the smoke.

b. Effects in Other Binders

Observations of other binders revealed basically the same trends as discussed for HTPB and CTPB, the differences being in degree rather than in kind. Polyurethane exhibited the least viscous boiling layer, appearing like water, and the least amount of char. Fluorocarbon exhibited the most viscous boiling layer, appearing like tar. The inclusion of catalysts



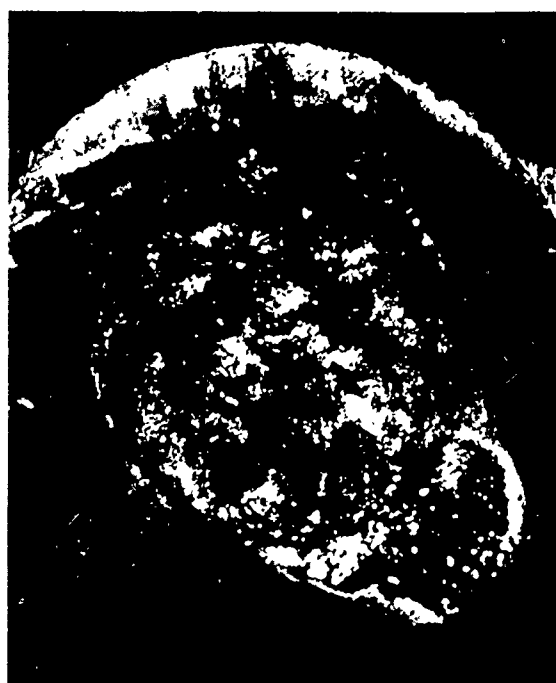
a. WITHOUT AP, 100 cal/cm²-sec, 1000 psi N₂



b. WITH AP, 100 cal/cm²-sec, 1 atm N₂



c. WITHOUT AP, 100 cal/cm²-sec, 1 atm Cl₂

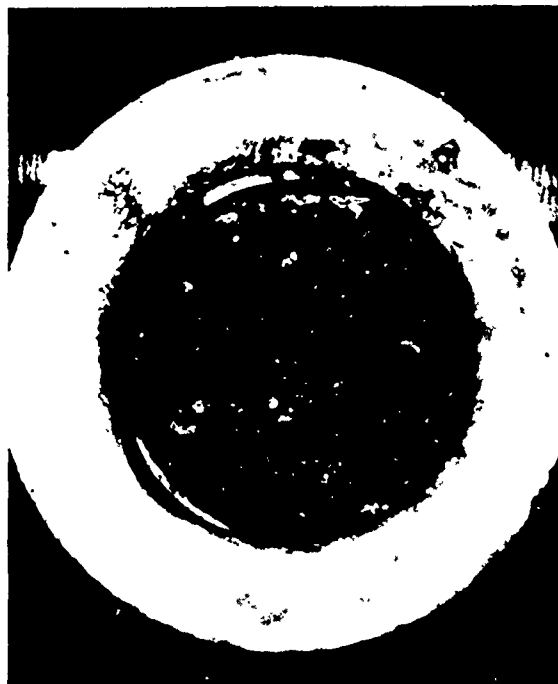


d. WITH AP, 100 cal/cm²-sec, 1 atm Cl₂

Figure 28 Post-Test CTPB Surfaces



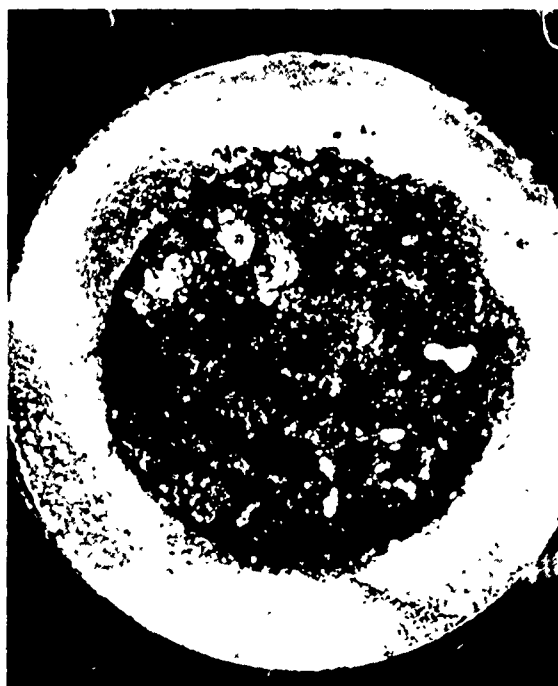
a. WITHOUT AP, 100 cal/cm²-sec, 1000 psi N₂



b. WITH AP, 15 cal/cm²-sec, 1 atm, N₂



c. WITH AP, 100 cal/cm²-sec, 1 atm, N₂



d. WITH AP, 100 cal/cm²-sec, 1 atm Cl₂

Figure 29 Post-Test HTPB Surfaces

in the HTPB did not affect the observations, except under combinations of high heat flux and pressure with AP, wherein micro-flames could be seen at the surface at random locations. The carborane binder was unique in that a whitish crust formed on the surface, appearing to change to a loose powder in the presence of AP. The micro-flames also appeared with AP in the carborane binder at high heat flux and pressure.

4. GAS SAMPLE ANALYSIS

Results for HTPB, CTPB, polyurethane, and fluorocarbon are listed in Table IV. Samples were acquired at $100 \text{ cal/cm}^2\text{-sec}$ and 1 atmosphere of N_2 . There are many similarities even though the binders are structured differently. The CTPB and polyurethane results appear to be virtually identical. Mass numbers 82 and 84 consistently show highest intensities. Although some mass numbers do not appear in all binders, many of them do so appear.

A surprising result is the absence of H_2O (mass number 18) and CO_2 (mass number 44) as major species from polyurethane, although CO_2 was detected from fluorocarbon. It was not possible to separate CO from N_2 (both number 28) because of the dominance of the N_2 . Hydrogen is not reported because the range of sensitivity for data acquisition did not encompass unity mass number. CH_3 and CH_4 (numbers 15 and 16) do not appear as major species, but CH_2 (number 14) does appear. Oxygen (number 16) was not detected from polyurethane, but fluorine (number 19) does appear from fluorocarbon. Major species appear to be heavy hydrocarbons, ranging from the C_3 to C_7 level, with the greatest variety evolved from HTPB.

A possible criticism of the sampling measurement is the length of time between the sampling and the measurement. Therefore, a comparison was made with flash mass thermal analysis data (43), wherein species are measured by a time-of-flight mass spectrometer as they evolve. Major species for HTPB at an arbitrary time are included in the table. Results are seen to be largely consistent with the pyrolysis sampling.

A kinetics measurement had been performed on mass number 43 from the flash mass thermal analysis data (43). This was one of the major species evolved, and represents a C_3 hydrocarbon fragment from higher hydrocarbons corresponding to monomers and oligomers expected from degradation of a butadiene polymer. The activation energy was 18 kcal/mole, not inconsistent with the pyrolysis result for HTPB. Such a low activation energy could be explained by a "weak-link" mechanism, associated with the splitting of terminal groups rather than molecular bond rupture.

5. THERMAL PROPERTIES

a. Components of Thermal Diffusivity

Thermal properties data at 70°F are summarized in Table V. The only thing really striking is that fluorocarbon has the lowest heat capacity and one of the highest conductivities, along with the highest density. However, thermal properties are not considerably different between the binders,

TABLE IV
RELATIVE SPECTRAL INTENSITIES OF
MAJOR BINDER PYROLYSIS PRODUCTS

<u>Mass Number</u>	<u>HTPB</u>	<u>HTPB (FMTA Major Species)</u>	<u>CTPB</u>	<u>Polyurethane</u>	<u>Fluorocarbon</u>
14	0.89	X	0.14	0.12	0.63
27	0.48	X	---	---	---
29	0.30	X	---	---	---
30	---	X	---	---	---
35	---	--	0.13	0.13	0.24
36	---	--	0.15	0.15	0.24
38	---	--	---	---	0.19
39	0.38	X	---	---	---
41	0.48	X	---	---	---
43	0.54	X	---	---	---
44	---	--	---	---	0.20
47	0.37	--	0.32	0.30	0.43
48	0.34	--	0.17	0.15	0.27
49	0.28	--	0.12	0.12	0.24
50	0.16	X	---	---	0.24
52	0.23	X	---	---	0.11
57	0.52	X	---	---	---
78	0.20	X	---	---	---
80	0.10	X	---	---	---
82	1.00	X	1.00	1.00	1.00
84	0.77	X	0.68	0.67	0.72
86	0.20	X	0.12	0.14	0.22
94	0.50	X	---	---	---
96	---	X	---	---	---
100	---	X	---	---	---

TABLE V
THERMAL PROPERTIES OF VARIOUS BINDERS

Binder	Heat Capacity (cal, gm-°K)	Thermal Conductivity (cal/cm-sec-°K)	Density (gm/cm ³)	Thermal Diffusivity (cm ² /sec)
CTPB (HC-434)	0.482	4.13×10^{-4}	0.915	9.35×10^{-4}
HTPB	0.434	4.41×10^{-4}	0.922	11.01×10^{-4}
Polyurethane	0.404	4.16×10^{-4}	1.007	10.17×10^{-4}
PBAN	0.423	5.35×10^{-4}	0.934	13.50×10^{-4}
Polysulfide	0.380	4.45×10^{-4}	1.272	9.22×10^{-4}
Telagen-S	0.483	4.15×10^{-4}	0.912	9.43×10^{-4}
Fluorocarbon	0.333	5.37×10^{-4}	1.604	10.02×10^{-4}

and thermal diffusivity falls within a relatively narrow range. There is a larger variation in density than in thermal properties.

b. Heat of Decomposition

Heat of decomposition was determined following the method of Shannon (25). An effective heat of decomposition is first determined by a plot of mass loss per unit sample area versus total energy supplied per unit sample area.

$$Q = a + (\Delta H_{\text{eff}})m$$

where

Q = energy supplied per unit area, heat flux multiplied by time

ΔH_{eff} = effective heat of decomposition, slope of plot

a = intercept of plot

m = mass loss per unit area

Then considering a heat balance at the pyrolyzing surface,

$$\Delta H_{\text{eff}} = C_s (T_s - T_o) + Q_L$$

where

C_s = binder heat capacity

T_s = equilibrium surface temperature

T_o = initial temperature

Q_L = heat of decomposition

In order to use this method most effectively, a heat flux should be selected to permit the greatest variation in the product of heat flux and exposure time. However, as discussed earlier in subsection 1.a., increasing the heat flux narrows the range of useful exposure times within the linear region. Another problem found to occur at high heat flux is the attenuation of heat flux actually received, due to unpurged smoke evolved from the binder. Although the radiometer was not affected by this smoke for the purpose of surface temperature measurement, uncertainty in the heat flux received would affect the energy balance. Applying the method to HTPB showed heat of decomposition to increase with increasing heat flux, with values becoming unrealistic above 100 cal/cm²-sec where smoke was detected in the movies. Applying the method to CTPB, which was less smoky at high heat flux, it was found that heat of decomposition increased relatively slightly

with increasing heat flux. Therefore, the standard flux condition was taken to be 35 cal/cm²-sec, where no smoke was seen in the movies and where the range of allowable exposure times was greatest.

The mass loss-energy plots for the various binders are combined in Figure 30. Carborane is not included because satisfactory data were not obtained without AP; with AP, the carborane line is close to the PBAN line. Polyurethane is seen to decompose at the highest rate for a given energy input, and fluorocarbon at the lowest rate.

Calculated heats of decomposition, Q_L , are summarized in Table VI. Polyurethane has the lowest value and fluorocarbon the highest. The range is proportionally greater than the range of thermal property values.

It is of interest to compare Figure 30 with Shannon's data. It is gratifying that the results for polyurethane, PBAN, and Butarez are consistent with his data. It also is of interest to compare the HC-434 CTPB with Butarez. Although their Arrhenius plots were very close, the HC-434 is observed to have a significantly higher regression rate and lower heat of decomposition.

It is also of interest to note that the University of Utah, measuring binder decomposition temperatures by differential thermal analysis in conjunction with a radiative heating source, indicated that polyurethane has the lowest decomposition temperature and fluorocarbon the highest (50). The values of decomposition temperature were lower than the surface temperature reported herein, consistent with the relatively low heating rates which they used.

TABLE VI
BINDER HEATS OF DECOMPOSITION

<u>Binder</u>	<u>Heat of Decomposition (cal/gm)</u>
CTPB (HC-434)	381
(Butarez)	519
HTPB	433
Polyurethane	260
PBAN	564
Polysulfide	530
Telagen-S	760
Fluorocarbon	1004

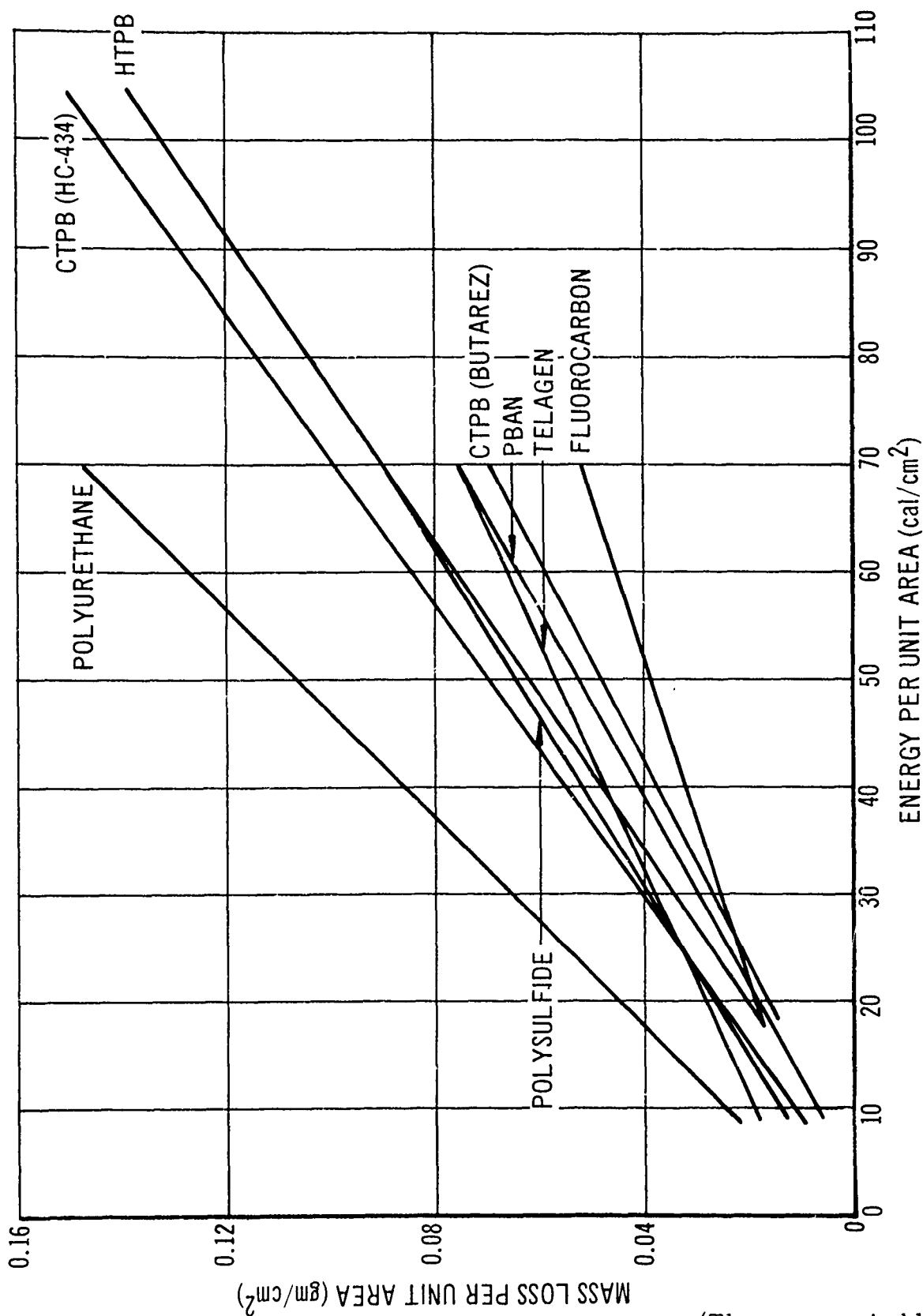


Figure 30 Mass Loss of Binders as a Function of Total Energy Input for a Heat Flux of 35 cal/cm²-sec

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SECTION VI

ANALYSIS

1. THE COMBUSTION MODEL

The manner in which the binder plays a role in determining burning rate, from a mechanistic standpoint, has been the subject of a previous hypothesis (10). Hypotheses concerning the role of binder encompass physical and chemical processes, kinetics, and energetics. Physical processes include the binder as inert interstitial spacing between oxidizer particles to impede the combustion front on the local microscopic scale, melting that would result in physical interference with oxidizer decomposition/combustion and therefore the ability of oxidizer to react with binder, heat transfer and phase changes, diffusion of binder decomposition products, and ramifications of the various processes that affect the physical geometry of the combustion zone. Chemical processes include binder pyrolysis, thermal and/or oxidative polymer degradation, and reactions between the products of binder decomposition with those of oxidizer decomposition/combustion in various regions of the gas phase. The kinetics and energetics that result from these processes serve to quantify the burning rate and the various details that relate to burning rate (e.g., surface temperature, flame heights, relative geometries of oxidizer and binder). These processes actually contribute to a total picture, and must be considered in that context. The extraction of an individual hypothesis of the role of the binder, with nothing more, has not yet provided the requisite binder information that would permit reconciliation of propellant combustion behavior.

The combustion model developed by Derr, Beckstead, and Price (16) attempted to include all of the foregoing processes in a reasonable manner, with the exception of a physical modeling of binder melting or of oxidative polymer degradation by interfacial heterogeneous reactions. It was felt that the importance of physical interference by melting, if any, was limited to special situations falling outside the realm of existing practical application: e.g., low concentration of fine AP in binders that melt more readily. Such a contention is, of course, subject to review. A physical model of interfacial heterogeneous reactions was dismissed because of a lack of experimental evidence; one such model was proposed by Hermance (44). Rather, if a binder decomposes by oxidative degradation instead of thermal degradation, it becomes a matter of incorporating the correct input constants in the model as presently providing for pyrolysis. The other processes were modeled to the extent that existing combustion knowledge warranted.

One of the purposes of this experimental program was to acquire the necessary data for practical binders with which to implement and further verify the combustion model. By combining model computations with knowledge of varying degrees of burning rate effects, the mechanistic role of binder can be better defined for future exploitation.

The binder-related input data necessary to implement the combustion model are as follows:

- Density, a known quantity
- Flame temperature, computed thermochemically for a known formulation
- Molecular weight of the gases, computed thermochemically
- Oxidizer/binder ratio for full stoichiometry, computed for a given formulation
- Molecular weight and oxidizer/fuel ratio for the species constituting the primary flame, calculable if these species are known
- Kinetics constants for the primary flame reaction, possibly determinable if the species are known
- Kinetics constants for binder pyrolysis, herein determined
- Binder heat of decomposition, herein determined
- Diffusion coefficient for the reacting gases, determinable if the species are known

A "standard" set of input data for all model parameters had been previously established for AP-polysulfide propellant, based upon available information, reasonable estimation, or model parametric optimization (16). Additional parameters were established for KP and HMX as oxidizers (45). It is evident that several of the binder-related parameters are routinely determinable, several others are measurable, and the remainder are difficult to quantify according to the state of knowledge of gas phase reaction processes. The first four listed fall within the routinely determinable category. The pyrolysis kinetics and heat of decomposition were to be measured on this program. The remaining parameters fall within the problem category.

Primary flame molecular weight and stoichiometry have, in past computations, been variously input by assuming a perchloric acid or chlorine oxide-hydrocarbon reaction, or merely by setting the values equal to those for the gross propellant. Fortunately, parametric computations revealed that these values have no significant effect. Data from this program, i.e., species evolved from the binder as sampled, would provide the possible identity of the fuel (e.g., mass number 82) for more precise determination were it necessary. Were this the fuel, and chlorine dioxide the oxidizer, then future flame studies could establish the primary flame kinetics, which are important model parameters.

At present, primary flame kinetics have been derived from the literature for other chlorine dioxide-hydrocarbon reactions. Similarly, knowledge of the fuel and oxidizer component distributions would enable a

computation of average diffusion coefficient. However, problems were encountered with respect to the computer program operation and results using the conventional form of the characteristic diffusional time (Equations 10a and 12a of Ref 16). Diffusion coefficient has since been bypassed by the "short diffusion flame" form of the expression (Equations 10b and 12b of Ref 16), wherein a proportionality constant was established by parametric optimization¹. The short diffusion flame form provided much better agreement between calculated and observed burning rate curves from the standpoint of position, shape, and effects of formulation changes, and more reasonable results with respect to calculated flame heights, etc, and their pressure-dependence (16).

2. APPLICATION OF DATA TO THE COMBUSTION MODEL

a. Hydrocarbon Binder Effects in Research Propellants

A summary of the requisite binder input constants is given in Table VII. Values are based upon the pyrolysis experiments in nitrogen, for which the most data were obtained.

A striking difference between these parameters and the previous "standard" polysulfide parameters exists with respect to the kinetics prefactor AF . In the units presented, the prefactor previously used was 2500 in association with an activation energy of 15 kcal/mole (16). Now, for an activation energy of 16.9 kcal/mole (HTPB), the prefactor is 299, which converts to an equivalent value of 157 for the same regression rate at 15 kcal/mole. In the case of polysulfide, the equivalent prefactor would be 19.5. In the case of fluorocarbon, it would be 2.3. Therefore, given a surface temperature, pyrolysis rates would be reduced by one to three orders of magnitude from the rate previously computed.

Another gross difference exists with respect to heat of decomposition. The "standard" value was 50 cal/gm. It is observed that the present values are higher by at least an order of magnitude.

As between binders, it is observed that there are significant differences in stoichiometry (fluorocarbon in particular), density, and flame temperature at 70-percent AP (this point is discussed further in the next subsection) as well as in kinetics. The 70-percent AP concentration corresponds to the "standard" concentration, and is the approximate concentration used in unmetallized unimodal research propellants (10, 16).

Computations performed for polysulfide, polyurethane, PBAN, HTPB, CTPB, and Telagen with the new constants resulted in the burning rate curves shown in Figure 31. All other constants were the standard constants, the inherent assumption being that the gas phase kinetics are independent of binder. Superimposed on the curves are data (10) except for Telagen.

¹ This is the "Y" parameter in the current program listing.

TABLE VII
BINDER INPUT CONSTANTS FOR THE COMBUSTION MODEL

	<u>Polysulfide</u>	<u>Polyurethane</u>	<u>CIPB</u>	<u>HTPB</u>	<u>PBAN</u>	<u>Telagen</u>	<u>Fluorocarbon</u>
AF (kinetics prefactor, gm/cm ² -sec)	5.6	49.4	12.8	299	270	7.3	2.6
E _a ¹ (kinetics activation energy, kcal/mole)	8.7	10.2	10.5	16.9	16.7	9.0	17.0
Q FUEL (heat of decomposition, cal/gm)	530	260	381	433	564	760	1004
BINDER DENSITY (gm/cm ³)	1.27	1.01	0.92	0.92	0.93	0.91	1.60
TF (flame temperature), 70% AP (°K)	2545	1787	1437	1451	1430	1446	2265
MOL WT (overall molecular wt), 70% AP	26.2	20.8	18.5	18.7	18.9	18.7	28.5
ST RAT (overall stoichiometric ratio) ^{1, 2}	28 (4.88)	36.6 (6.15)	82.8 (9.53)	79.7 (9.30)	78.2 (9.00)	80 (9.30)	3.1 (1.50)

¹ Under the present computer format, the AP/binder ratio at stoichiometry is not input directly. The tabulated numbers result from an additional computation. The program has since been modified to accept AP/binder ratio at stoichiometry directly. The numbers in parentheses are AP/binder ratio at stoichiometry.

² PRI MOL WT and PRI ST RAT (analogous primary flame properties) were set equal to MOL WT and ST RAT, respectively.

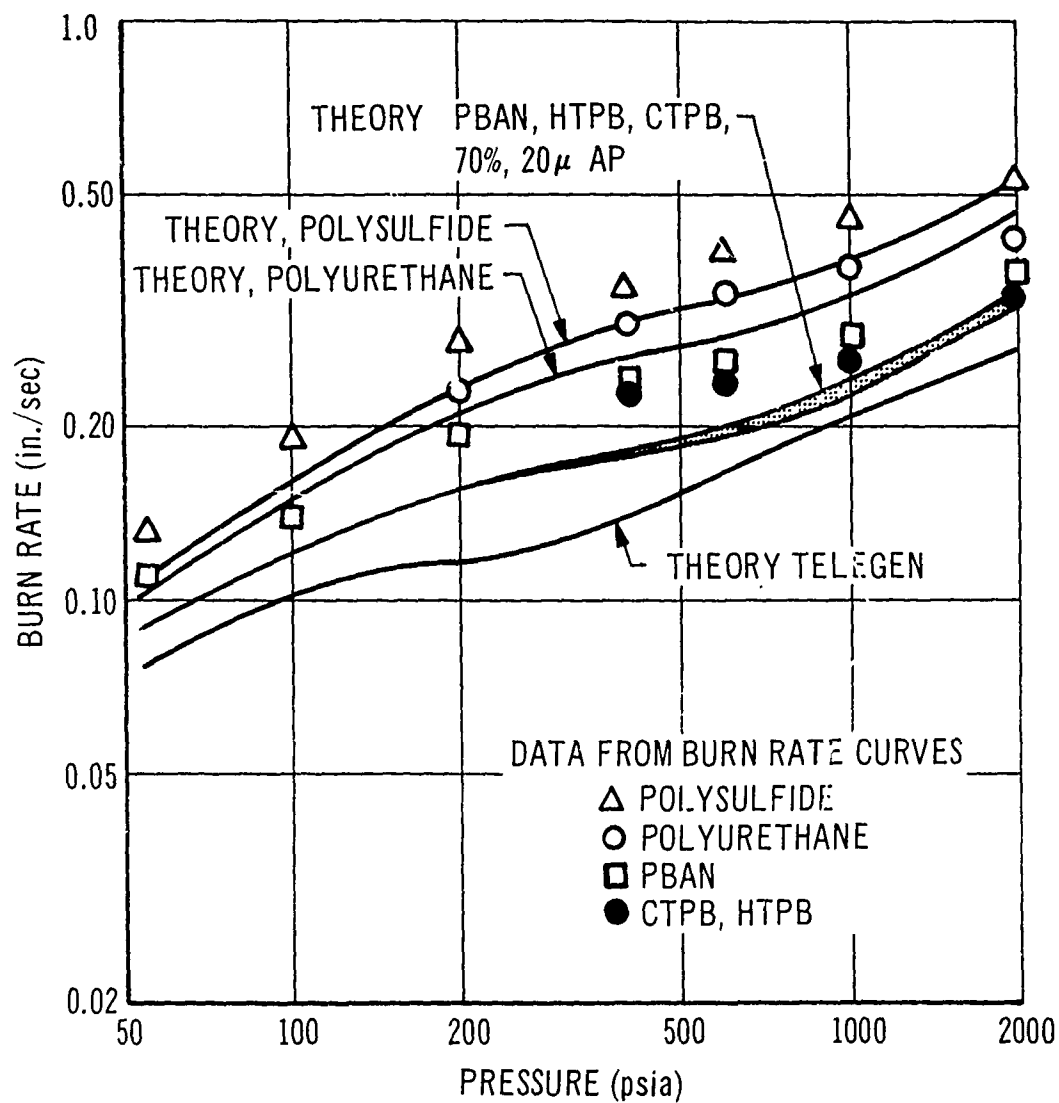


Figure 31 Combustion Model Predictions with New Binder Constants

It is observed that the relative positions of the burning rate curves are correctly predicted, but the exact positions of the curves are somewhat low. Thus, in the case of the polysulfide standard, the effect of the new constants was a reduction in burning rate, but not even remotely proportional to the magnitudes of the changes in the constants. The polysulfide is correctly predicted to have the highest burning rate, then polyurethane, and then a close grouping of PBAN, HTPB, and CTPB. Data for a Telagen formulation of this type were not available; however, the general character of the lower burning rate (based upon "practical" formulations) does appear.

The relative positions of the burning rate curves correlate well with flame temperature. Polysulfide has the highest flame temperature, then polyurethane, and then CTPB, HTPB, and PBAN as a close group. Indeed, in prior work with the model, flame temperature has been found to be an influential parameter. The lower position of Telagen appears to be a consequence of its relatively high heat of decomposition; Telagen is not significantly different in other respects. It appears that binder pyrolysis kinetics do not impact burning rate.

The new binder kinetics constants did have one significant impact upon the model results, which introduces a question bearing upon model validity. The reason why the gross changes in the constants, from the old standard values to the new values, did not appreciably affect burning rate was evidenced by the output surface structure. The AP was predicted to be fully recessed into the binder, to the limit of statistical possibility, under almost all conditions; i. e., the output values of HDP and HDN¹ were pegged on their negative limits. The physical significance is that, with the new constants, the local regression rate of the binder is so much lower than that of the AP that the model cannot predict a statistical surface structure consistent with burning rate and the uniform surface temperature assumption. The implication is that the uniform surface temperature assumption is incorrect; the binder in fact has a higher surface temperature than the AP. With the old constants, the AP was predicted to protrude at low pressures, becoming flush with the binder at intermediate pressures and eventually recessed at high pressures, in accord with Bastress' experimental observations (46). With the new constants, the effect of pyrolysis kinetics on the statistical surface structure is eliminated, and hence an effect on burning rate would not appear.

To further examine the consequence of pyrolysis kinetics, the old constants were restored and parametric computations were made, with variations in the kinetics prefactor. By restoring the old constants, the impact of the pyrolysis kinetics on surface structure would be restored, so that the resultant effect on burning rate could be observed. This also would serve to approximate a two-temperature model with the new constants, in the sense that the binder surface is hot enough that its relative rate of

¹ Statistical heights of the AP surfaces relative to the binder surfaces

regression would be as before. The kinetics prefactor was varied from 1000 to 5000, the standard value being 2500. As expected, increasing the prefactor tended to make the AP protrude more at a given pressure (the binder now becomes relatively fast). However, the burning rate varied by only 10 percent over this range of prefactor. Therefore, the impact of pyrolysis kinetics is mainly upon the statistical surface structure and not upon the burning rate.

The experimental data revealed no effect of catalysts on the pyrolysis kinetics in nitrogen and with AP; in any event, the model appears to show that pyrolysis kinetics have little impact upon burning rate. Therefore, it would be concluded that these particular catalysts do not manifest themselves by changing the process of binder pyrolysis.

Similarly, the high burning rate of carborane propellant could not be explained by surface processes. The pyrolysis rate was even slower than for the binders discussed above.

Also, the impact of the chlorine environment would not be predicted to have an effect on computed burning rates. The chlorine in general appeared to slow down the surface kinetics, and where it speeded them it did not do so to a degree that would noticeably affect burning rate.

b. Consequences of Research Propellants

Although "research" propellants are useful for experimentation for the purpose of improved combustion knowledge, their limitations must be recognized as well in applying the information gained to "practical" propellants.

For example, the result that polysulfide and polyurethane propellants have higher burning rates than CTPB propellants is not generally true in "practical" propellants. What happens in an unmetallized propellant containing 70-percent AP is that the burning rate will be sensitive to binder stoichiometry. The oxidizer contents of polysulfide and polyurethane enable them to have considerably higher flame temperatures at 70-percent AP. Practical propellants of 86-percent solids loading, and with aluminum, will not show these kinds of temperature differences. Moreover, polysulfide and polyurethane will encounter solids loadings limitations before CTPB will, further narrowing the differences in flame temperature and in some cases reversing them. Consequently, trends at one oxidizer concentration need not be representative of trends in practical propellants. Such can be the case with respect to any single model parameter or propellant parameter.

Another consequence of research propellants, specifically low AP concentration amenable to the use of uninodal particle size, is the observance of plateau and mesa behavior sometimes leading to extinguishment at intermediate pressures. Originally associated with polyurethane and attributed to its relative ease of melting, the phenomenon also has been observed in polysulfide, PBAA, polyisobutylene, and polyvinylchloride (10, 47). Observations made on this program have established that melting is not unique to polyurethane; all of the binders melt and boil to some degree.

The curves of Reference 16, and the curve for Telagen in Figure 31, imply that the present model does have the potential for showing plateau or mesa behavior at sufficiently low AP concentrations and burning rates. To verify this point, computations were performed for 65-percent AP in polyurethane. Results are shown and compared to the 70-percent AP results in Figure 32. A mesa does appear at the lower concentration, and without resort to a physical interference melt mechanism. The result appears to stem from a stronger manifestation of the diffusion process responsible for the decrease in pressure exponent with increasing pressure (prior to the high pressure regime where the AP begins to take over). As diffusion becomes more difficult, with increasing pressure or because the concentration of AP is reduced, gas phase effects are mitigated and the propellant burning rate curve begins to approach the AP burning rate curve. Eventually, with diffusion depressed further, the approach to the AP curve takes the form of a plateau and, ultimately, a mesa. It appears analogous to the loss of catalysis in double-base propellant, wherein the catalyzed burning rate curve approaches and merges with the uncatalyzed curve with increasing pressure (10). Although consequences of a melt cannot be ruled out, it is noteworthy that the phenomenon can be explained by diffusion.

c. Fluorocarbon Binder Effects

Fluorocarbon propellant burning rates are unique not only with respect to the relatively low burning rate and high pressure exponent, but also in the relative independence of burning rate on particle size and relative ineffectiveness of the usual catalysts. The fluorocarbon propellant further proved to be unique in terms of the computer program response to the input constants associated with it.

The first computation was exited from the computer without results. A set of forced computations resulted in the predictions of very high burning rate, pressure exponent greater than unity, unrealistically high values of AP surface temperature, and that a 200-micron AP propellant burns faster than a 20-micron AP propellant. The two particle sizes were used to see if the relative independence on particle size would be predicted. The computer program also output negative flame heights, the height being more negative for the larger particle size. The problem was found to occur in the diffusion flame equations.

The basic diffusion flame equation appears as Equation 13 in Reference 16. It results from a modification of the Burke-Schumann diffusion flame analysis as suggested by Williams (48). The diffusional mixing length appears as a function of terms related to AP particle size and concentration, AP/binder density ratio, and a term (η) that additionally includes a dependence upon the stoichiometric AP/binder ratio. If a certain inequality is satisfied in the expression for η , η will become negative, which can render the flame height negative. It was found that the uniquely low stoichiometric ratio associated with fluorocarbon was responsible for producing this inequality; fluorocarbon has a substantial oxidizer content.

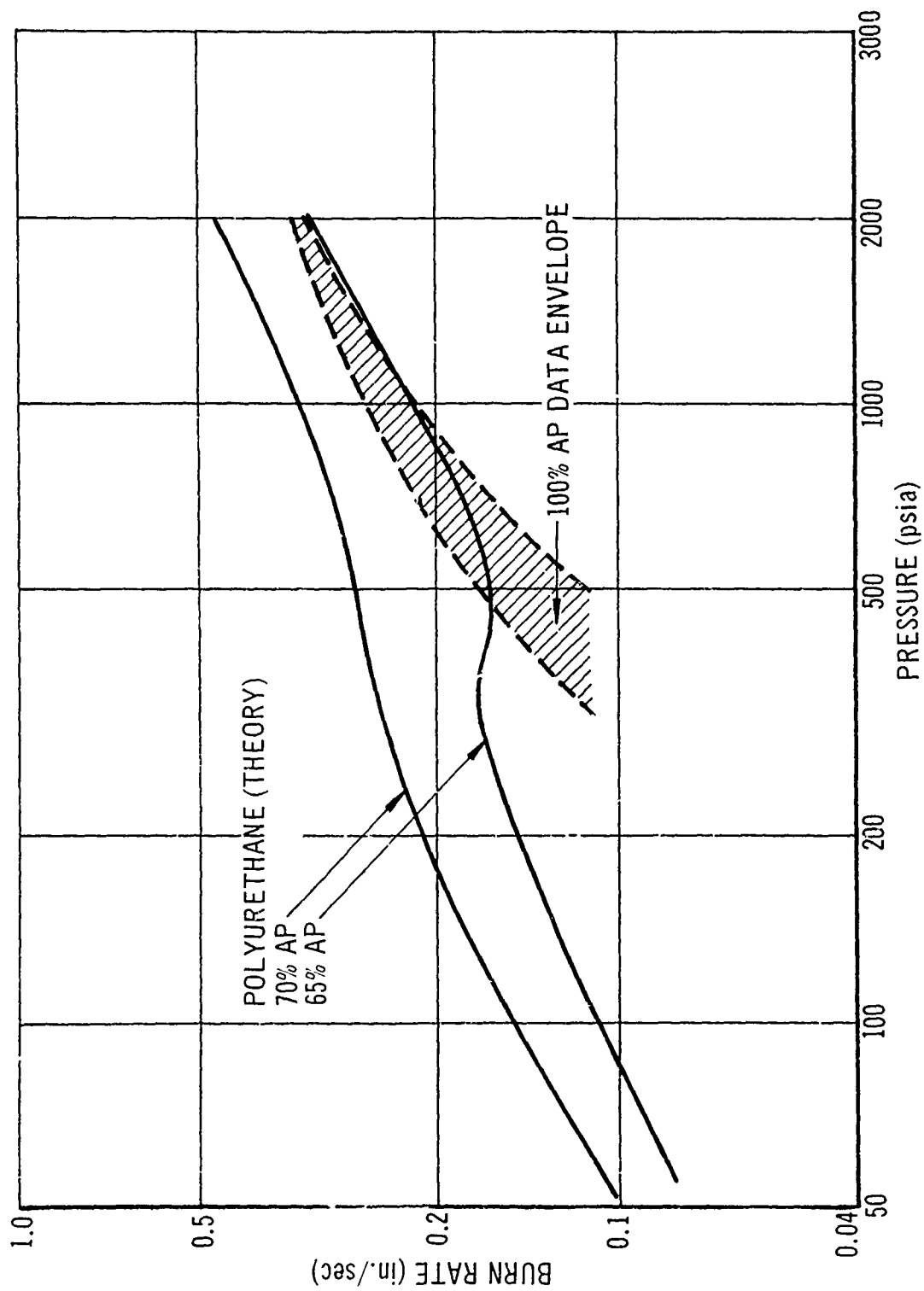


Figure 32 Effect of Ammonium Perchlorate Concentration on Burning Rate, Showing Mesa Behavior with Present Binder Constants

The diffusion flame analysis does not distinguish between a solid surface and a gas phase as such; it is really a coaxial stream bunsen-burner type of analysis, with dimensions related to the microscopic characteristic dimensions of a composite propellant (AP particle size and binder interstitial spacing). The zero distance dimension would correspond to the rim of the burner. In the framework of the model, a certain combination of parameters will result in essentially a premixed flame, but the equations can enter a physically forbidden regime. If the mixing distance is computed to be negative, and greater in absolute magnitude than the reaction distance, the flame height will be computed negative. Because the mixing distance is also tied to AP particle size through Equation 12b of Reference 16, a larger size will show a more negative distance.

Interpreting the physical significance of the result to be a premixed flame, a statement was put into the program forcing a finite positive mixing distance in the event that the diffusion flame equations calculate a negative distance. This is analogous to pegging HDP and HDN on their statistically possible limits. Calculations were repeated, with the results shown in Figure 33. The predicted burning rate is high by about a factor of two, but the character of the pressure exponent and the independence of burning rate with respect to particle size both correctly appear.

This result is most interesting. It shows a case of where and why the statistical geometry (particle size and surface area) provided by the AP does not manifest itself to affect burning rate. Because catalysts are not effective in fluorocarbon, an inference is drawn that the mechanism of catalysis in hydrocarbon may be associated with reaction rates affecting surface area. This inference is not conclusive because there are alternative possibilities, e.g., the catalyst does not accelerate the primary flame reaction in fluorocarbon propellant.

The high predicted magnitude of the burning rate is not of concern in view of the arbitrary selection of a finite mixing distance and the assumption that primary flame kinetics are independent of binder in these sets of computations. What is of concern is the questionable applicability of the present diffusion flame model to inert binders containing appreciable oxidizer in their structure. In the extreme, it never was stipulated that the model would apply to a double-base or reactive binder, which introduces new flame as well as diffusion considerations.

d. Assessment of Model Deficiencies

The two major model deficiencies uncovered in this program are the indicated need for a two-temperature model (allowing oxidizer and binder to have different surface temperatures) and for a reexamination of the diffusion flame model in view of stoichiometry effects.

That binder pyrolyzes at higher surface temperatures than AP is supported by the experimental data on this program, experimental data in the area of insulation technology (49), and the result of applying the kinetics data to the model where the binder is assumed to have the same surface

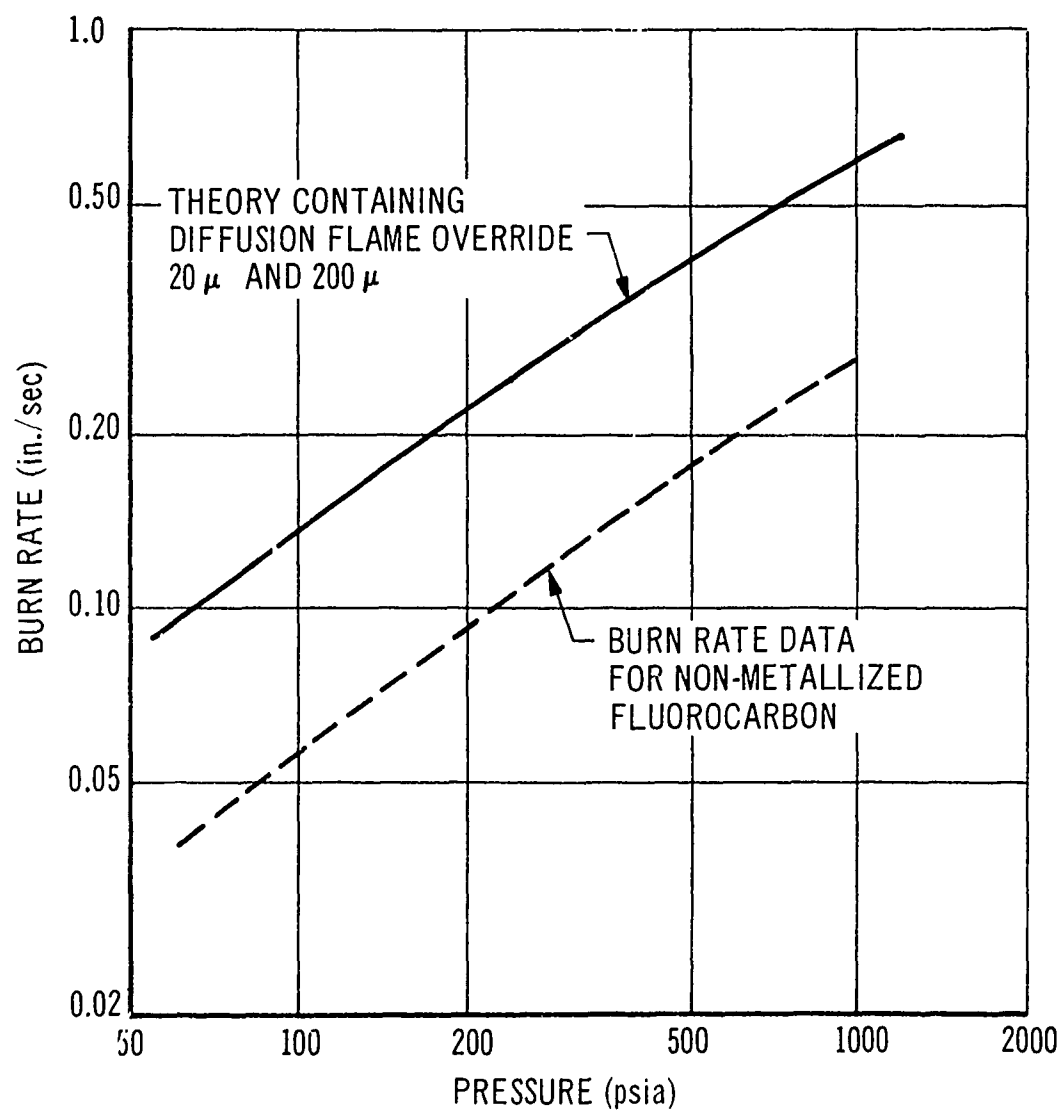


Figure 33 Fluorocarbon Propellant Burning Rate

temperature as AP. Supplementary calculations indicate, however, that a two-temperature model would do nothing more than correctly show the surface temperatures and surface structures because the binder surface processes were shown to have only a minor effect on burning rate.

Similarly, with regard to binder melting, a physical modeling of the melting would be of little consequence if all binders melt and the effect as a surface process on burning rate is minor. Plateau and mesa behavior observed in certain research propellants appeared to be adequately explained by gas phase diffusion effects.

The diffusion flame deficiency uncovered in applying the model to fluorocarbon was summarily corrected by a premixed flame override that would apply whenever the equations enter a physically forbidden regime. Although this correction resulted in predicting the character of fluorocarbon propellant burning rate properties, it should not be considered a substitute for a reexamination of the diffusion flame model premises. Perhaps the time is ripe for extending the model to apply to reactive binders, wherein such reexamination would be a necessary task.

In summary, the model deficiencies uncovered do not appear to be of a nature that would impair the applicability of the model to composite propellants. The model continues to be a useful combustion research tool.

3. RELATION OF UNIQUE BINDER PROPERTIES TO BURNING RATE TRENDS

a. Binder Structure

Binder structure per se does not correlate with burning rate trends in that significant changes in binder structure may or may not produce major burning rate effects. Significant changes in structure are found between polysulfide, polyurethane, and polybutadiene, and between PBAN and CTPB within the polybutadiene family, yet burning rate effects are not major. On the other hand, major burning rate effects are produced by fluorocarbon, carborane, or carboranesiloxane. Therefore, it can be argued that CF_2 groups tend to depress burning rate whereas boron, borane, or silicon tend to increase burning rate. The incorporation of boron or iron compounds within the polymer structure is not a novel approach.

b. Flame Temperature

Flame temperature definitely corresponds with burning rate in hydrocarbon propellants formulated to show significant flame temperature differences. However, these differences are mitigated in practical propellants. The correlation is also upset by fluorocarbon, which yields low burning rates notwithstanding high flame temperature at low AP concentrations. Increasing AP concentration in fluorocarbon is counterbalanced by a reduction in flame temperature because of the unique stoichiometry, so that the burning rate remains low in those oxidizer-rich propellants having practical application (3).

c. Pyrolysis Kinetics

No appreciable difference in pyrolysis kinetics was observed between HC-434 and Butarez versions of CTPB. Therefore, molecular weight or extent of the polymer chain does not appear to affect the pyrolysis mechanism.

Differences in pyrolysis kinetics were observed between CTPB and HTPB, indicating an effect of termination; however, values of $E/\log A$ were comparable. A similar situation applies to binder saturation, in comparing HTPB with Telagen.

PBAN and HTPB were nearly identical notwithstanding differences in polymer structure. However, polysulfide, polyurethane, fluorocarbon, and carborane showed significant differences from HTPB or CTPB.

Probably the most interesting result is the similarity between fluorocarbon and carborane because these two materials represent extremely opposite burning rate effects. The similarity was in the relatively high $E/\log A$ compared to all of the other binders. Therefore, a sluggish binder does not necessarily imply a low-burning-rate propellant.

The inclusion of catalysts in HTPB did not significantly affect the pyrolysis results, except in chlorine, but this may have involved flame processes. Nor were the results affected by combining AP with catalysts, except for ignitions at high heat flux and pressure. However, including AP in carborane mitigated the appearance of a whitish char that formed in the absence of AP, evidencing some interaction.

It therefore appears that binder pyrolysis kinetics do not correlate with burning rate trends. Moreover, the differences in kinetics observed between similarly structured binders, and the similarities observed between some of the differently structured binders, taken together suggest that the thermal decomposition mechanism is a physical process such as the boiling seen in the movies.

d. Pyrolysis Products

Polybutadiene, polyurethane, and fluorocarbon evolved a similar array of pyrolysis products notwithstanding differences in polymer structure. Mass numbers 82 and 84 consistently dominated the spectrum. Any uniqueness of fluorocarbon would be associated with fluorinated species; mass number 38 (F_2 ?) was unique to fluorocarbon.

e. Thermal Properties

Except for the relatively high heats of decomposition for Telagen and fluorocarbon, heat of decomposition does not consistently correlate with burning rate. Other thermal properties are not appreciably different between the binders.

f. Stoichiometry

Fluorocarbon exhibits a unique oxidizer content and low burning rate. However, any effect of the oxidizer content would have to be assigned to the fluorine because of the lack of unique effects in polysulfide and polyurethane, which contain more oxygen relative to polybutadiene. In the case of the hydrocarbons, stoichiometry effects can be related to flame temperature effects. However, this relation does not hold true for fluorocarbon.

SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

1. CONCLUSIONS BASED ON EXPERIMENTAL DATA

- (1) Binders of practical interest to solid rocket propulsion exhibit a molten, boiling surface intermingled with carbonaceous char over a wide range of heating rates and pressures. The addition of ammonium perchlorate, or the imposition of a chlorine gas environment, increases the extent of char formation. Carborane exhibits a unique whitish char, which becomes a reduced amount of loose powder in conjunction with AP.
- (2) The kinetics of binder pyrolysis are independent of heat flux, pressure, the presence of AP, and the presence of catalysts over the range of ingredients and conditions tested. The kinetics do appear, however, to be significantly affected by an oxidizing gas environment, subject to the possibility of gas phase reactions occurring in the experiments.
- (3) The different binders exhibit a range of kinetics constants, but activation energy does not exceed 17 kcal/mole, suggesting a weak-link degradation mechanism or the physical process of boiling observed. Measured surface temperatures cover a broad range, from 768°C for polyurethane to 2550°C for fluorocarbon at a heat flux of 200 cal/cm²-sec.
- (4) Major gaseous pyrolysis products are relatively constant between the binders tested. The products are consistently dominated by mass numbers 82 and 84, probably heavy hydrocarbon fragments.
- (5) Thermal properties are relatively constant between the binders, but heat of decomposition varies from 260 cal/gm for polyurethane to 1004 cal/gm for fluorocarbon.

2. CONCLUSIONS BASED ON APPLICATION OF THE DATA TO THE COMBUSTION MODEL

- (1) The role of binder in solid propellant combustion does not appear to take place through surface pyrolysis processes. The approach to major combustion tailoring should be directed toward gas phase processes.
- (2) The model predicts burning rate trends observed in research hydrocarbon propellants; however, the effect of binder in those propellants is dominated by flame temperature effects that are mitigated in practical propellants. Mesa behavior, also mitigated in practical propellants, is predicted to stem from a diffusion effect.

- (3) The model indicates that unique burning rate properties of fluorocarbon propellant stem from the effect of its unique stoichiometry on diffusional processes in the gas phase.
- (4) The model could not predict catalytic effects from the data acquired on this program since there were none that impact the model. The inference is that catalysts affect AP processes, or gas phase reaction processes involving AP and binder decomposition products, and not the binder per se.
- (5) The uniform surface temperature assumption of the model is open to question; binder surface temperatures can be higher than AP surface temperatures. However, effort to develop a two-temperature model would have questionable value because of the relative lack of importance of binder surface processes. The surface processes influence the predicted surface structure, but the effect in turn on burning rate is minor. Nevertheless, the predictions will be more consistent and realistic.
- (6) The diffusion flame model is of questionable applicability to inert binders containing appreciable oxidizer in their structure; the model enters a physically forbidden regime with fluorocarbon, but not with polysulfide or polyurethane. Effort involving a reexamination of the diffusion model in this respect would be more fruitful if made part of an effort to extend the model to apply to active binders. Fluorocarbon behavior was correctly predicted here by merely blocking the forbidden regime with a program statement.

3. CONCLUSIONS BASED ON CORRELATING DATA AND BINDER PROPERTIES WITH KNOWN BURNING RATE EFFECTS

- (1) Without the use of a combustion model, burning rate trends could be correlated with flame temperature; but this correlation is limited to research-type hydrocarbon propellants (i. e., low AP concentration amenable to unimodal particle size, and without metal).
- (2) The high burning rates achievable with catalytic materials could not be rationalized by data acquired on this program, except possibly by the occurrence of ignition with AP at high heat flux and pressure or by results in chlorine.
- (3) The low burning rates associated with fluorocarbon could be related to its unique heat of decomposition; fluorocarbon is also unique with respect to stoichiometry and the presence of fluorine bound in an inert polymer.
- (4) Burning rate trends could not be correlated by pyrolysis kinetics properties, and kinetics properties could not be correlated with polymer structure, again suggesting that

molecular bond rupture is not the principal mechanism. Fluorocarbon and carborane, both having thermal resistance applications, exhibit similar pyrolysis rate effects.

- (5) The unique whitish material formed by the carborane binder is the only unique property that it exhibited, and is possibly relatable to the high burning rate property.

4. RECOMMENDATIONS

Based upon the data acquired on this program, and combustion model results, it appears that the role of inert binder in composite propellant combustion is principally as follows:

- (1) To absorb combustion energy according to its heat of decomposition
- (2) To supply species to the gas phase reaction zones and thereby influence gas phase diffusion processes and reaction rates
- (3) To determine the flame temperature of the propellant

Of these three effects, the gas phase reaction processes have the greatest potential for bringing about major combustion changes in practical propellant formulations. In formulations containing high solids loading and metal, flame temperatures will not vary significantly with binder type (subject to future technological innovations). Parametric studies with the model show that the primary flame reaction rate is much more influential than binder heat of decomposition. The inference is that major binder effects presently known, ranging from carborane or other catalytic materials (high burn rate) to fluorocarbon (low burn rate), stem at least in part from the kinetics of the primary flame.

It is therefore recommended that future studies be directed toward a detailed investigation of the role of binder in the primary flame. This could take the following form:

- Phase I:
- (1) Conduct a more extensive study of binder pyrolysis products, including
 - (a) Greater emphasis on flash mass thermal analysis (FMTA), to obtain the timewise formation of species
 - (b) More extensive data analysis to establish the parent compounds as well as the major species
 - (2) Repeat the above testing with increasing concentrations of AP, with and without the known catalysts, to
 - (a) Observe the changing product distribution

- (b) Observe what happens to the major binder pyrolysis products
- (c) Deduce from the above the governing reactants
- (3) Perform fundamental flame studies, as have been performed with HClO_4 , ClO_2 and light hydrocarbon gases, but instead using the measured heavy species representative of binder pyrolysis, to quantify the kinetics; compare with FMTA

Phase II: Continue the above experiments to learn how to control the rates of these gas phase reactions

- (a) Known catalytic reagents
- (b) New ingredients suggested by the information acquired
- (c) Novel approaches, including polymer tailoring

Phase III: Incorporate this knowledge into a propellant

- (a) Initially, a practical binder may not result and should not be expected
- (b) In association with the polymer industry, develop the approach into a practical binder.

SECTION VIII

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13. ABSTRACT The objective of this program was to investigate and define the effects of inert binder properties on composite solid propellant burning rate. Experimental pyrolysis data were obtained for many binders of practical interest over a wide range of heating rates and pressures, in several environmental gases, with and without 10-percent ammonium perchlorate (AP) contained in the sample, and in some cases with catalysts. These data were used to extract kinetics constants from Arrhenius plots, and heat of decomposition. In addition, motion pictures were taken of the pyrolyzing surface and gas samples were extracted for analysis. Pyrolysis kinetics varied between binders, but were found to be independent of pressure, the presence of AP, and the presence of burn rate catalysts; however, a chlorine gas environment had a material effect upon the results. All of the binders exhibited molten, boiling surfaces mingled with char, to varying degrees; the amount of char increased with AP present, and in chlorine. Relevant data were input to the Derr-Beckstead-Price combustion model in order to associate binder properties with known binder effects on burning rate. Although the effects were predictable, they stemmed from properties other than pyrolysis kinetics; however, the binder data as applied to the model revealed possible deficiencies in the model which are discussed. It appears that the approach of combustion tailoring by binder modification would have to involve the gas phase combustion processes rather than surface pyrolysis. Therefore, future work concerning the role of binder should be directed toward the gas phase.			

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